(SIPO)

Title: Single-piece ceramic electronic element and mfg. method thereof, ceramic paste and mfg. method thereof


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## Abstract


A process for producing a monolithic ceramic electronic component, which includes: providing a ceramic slurry, a conductive paste, and a ceramic paste; forming a plurality of composite structures each comprising a ceramic green sheet produced by shaping the ceramic slurry,

internal circuit element films formed by applying the conductive paste partially onto a main surface of the ceramic green sheet so as to provide step-like sections, and a ceramic green layer which compensates for spaces defined by the step-like sections, the ceramic green layer being formed by applying the ceramic paste onto the region on the main surface of the sheet on which the element films are not formed, so as to substantially compensate for the spaces; forming a green laminate by laminating the composite structures; and firing the green laminate. A monolithic ceramic electronic component which is produced through the process; a ceramic paste; and a production process for the paste are also disclosed.

2357373 Monolithic Ceramic Electronic Component and Production Process

Therefor, and Ceramic Paste and Production Process Therefor

## BACKGROUND OF THE I-NVENTION

### Field of the Invention

The present invention relates to a monolithic ceramic electronic component and a production process therefor, and to a ceramic paste and a production process therefor. More particularly, the present invention relates to a monolithic ceramic electronic component comprising internal circuit element films formed between ceramic sheets, and ceramic layers which compensate for spaces defined by step-like sections which are formed by the internal circuit element films, each ceramic layer being formed so as to have a pattern negative to that of the corresponding film, and a production process for the component; and to a ceramic paste which is advantageously employed for fori-ning the ceramic layer, and a production process for the paste.

### Background Art

When a monolithic ceramic electronic component, such as a monolithic ceramic capacitor, is produced, a plurality of ceramic green sheets are provided and the sheets are then laminated. In accordance with the intended function of the monolithic ceramic electronic component, an internal circuit element film, such as a conductive film or a resistive film, is formed on a specific ceramic green sheet, the film being an element of a capacitor, a resistor, an inductor, a varistor, a filter, etc.

In recent years, miniaturization and weight reduction of electronic devices such as mobile communication devices have been progressing. For example, when a

monolithic ceramic electronic component is employed as a circuit element in such an electronic device, the size and the weight of the electronic component must be reduced. For example. there has been increasing demand for a monolithic ceramic capacitor of small size and large capacitance.

A typical process for producing a monolithic ceramic capacitor is as follows.

Dielectric ceramic powder, an organic binder, a plasticizer, and an organic solvent are mixed together, so as to prepare a ceramic slurry. The resultant ceramic slurry is 19 shaped into a sheet having a thickness of some tens of Vim, by means of a doctor-blade method or a similar method on a support, such as a polyester film, which is coated with a silicone resin serving as a peeling agent, to thereby form a ceramic green sheet, and the sheet is then dried.

Subsequently, onto a main surface of the ceramic green sheet, a conductive paste is applied through screen printing, so as to have a plurality of patterns which are separated from one another. Thereafter, the resultant sheet is dried, to thereby form internal electrodes serving as internal circuit element films on the sheet. Fig. 7 is a plan view of a portion of a ceramic green sheet 2 on which internal electrodes 1 are formed so as to be distributed at a plurality of positions as described above.

Subsequently, the ceramic green sheet 2 is peeled off the support, and then cut into pieces of appropriate size. Thereafter, predetermined amounts of the pieces are laminated as partially shown 'In Fig. 6. Furthermore, predetermined amounts of ceramic green sheets not containing internal electrodes are laminated on opposite surfaces of the resultant laminate, to thereby form a green laminate 3.

The green laminate 3) is pressed in a vertical direction with respect to a horizontal plane. and then cut into laminate chips 4 as shown in Fig. 8, the chips being of appropriate size so as to be employed as individual monolithic ceramic capacitors.

Subsequently, the binder is removed from each of the chips, the resultant chip is fired, and then external electrodes are formed on the chip, to thereby produce a monolithic ceramic capacitor.

In order to reduce the size of such a capacitor and increase the capacitance thereof, the ceramic green sheets 2 and the internal electrodes 1, which are laminated, must be increased in number, and the ceramic green sheets 2 must be thinned.

However, when the laminated sheets and electrodes are increased in number and the sheets are thinned as described above. the internal electrodes 1 are accumulated. Cofisequently, difference in thickness becomes more apparent between a portion at which the electrodes 1 are provided and a portion at which the electrodes 1 are not provided; or a portion at which relatively large amounts of the internal electrodes 1 are provided in a vertical direction with respect to a horizontal plane and 3 a portion at which small amounts of the electrodes 1 are provided in the vertical direction. Therefore. for example, as shown in Fig. 8, the appearance of the resultant laminate chip 4 is deformed such that a main surface of the chip assumes a convex shape.

When the laminate chip 4 is deformed as shown in Fig. 8, a relatively large strain arises during pressing at the portion at which the intemal electrode 1 is not provided or the portion at which relatively small amounts of the electrodes 1 are provided in a vertical direction with respect to a horizontal plane. In addition, adhesion between the ceramic green sheets 2 is lowered, and a structural defect such as delamination or microcracking tends to occur, the defect being caused by internal stress of the chip during firing.

When the laminate chip 4 is deformed as shown in Fig. 8, the internal electrode 1 is undesirably deformed, which may cause a short circuit.

The aforementioned problems may lower the reliability of the resultant monolithic ceramic capacitor.

In order to solve the aforementioned problems, for example, Japanese Patent Application Laid-Open (kokai) Nos. 56-94719, 3-74820, and 9-106925 disclose a method in which a ceramic green layer 5 is formed on a region of a ceramic green sheet 2 on which internal electrodes 1 are not formed, as shown in Fig. 2, to thereby substantially compensate for spaces defined by step-like sections

which are formed by the internal electrodes 1 on the ceramic green sheet 2.

As described above, in the case in which the ceramic green layer 5 which compensates for spaces defined by the step-like sections is formed, when a green laminate 3a is formed as partially shown in Fig. 1, there is no substantial difference in thickness between the portion at which the electrodes 1 are provided and the portion at which the electrodes 1 are not provided; or between the portion at which relatively large amounts of the internal electrodes 1 are provided in a vertical direction with respect to a horizontal plane and the portion at which small amounts of the electrodes 1 are provided in the vertical direction. Therefore, as shown in Fig. 3, the resultant laminate chip 4a tends not to be undesirably deformed as shown in Fig. 8.

4_ Consequently. the aforementioned structural defect such as delamination or micro cracking; or short circuit due to deformation of the internal electrode 1 tends not to occur, thereby enhancing the reliability of the resultant monolithic ceramic capacitor.

The aforementioned ceramic green layer 5 which compensates for spaces defined by the step-like sections has a composition similar to that of the ceramic green sheet 2, and the layer 5 is formed by applying a ceramic paste containing dielectric ceramic powder, an organic binder, a plasticizer, and an organic solvent onto the green sheet 2. In order to form the layer 5 through printing at high accuracy so as to attain a thickness (e.g., 2 pm or less) which is equal to that of the internal electrode 1, dispersibility of the ceramic powder in the ceramic paste must be high.

In connection with the foregoing, for example, Japanese Patent Application Laid-Open (kokai) No. 3-74820 discloses a method for preparing a ceramic paste in which ceramic powder is dispersed by use of a three-roll mill. However, it is difficult to increase dispersibility of the ceramic powder through use of a three- roll mill only.

Japanese Patent Application Laid-Open (kokai) No. 9-106925 discloses that a ceramic slurry for forming a ceramic green sheet 2 is prepared by mixing dielectric ceramic powder.. an organic binder, and a first organic solvent having

a low boiling point, and the resultant slurry is employed for forming a ceramic green sheet 2; and that the slurry is mixed with a second organic solvent having a boiling point higher than that of the first organic solvent, and the resultant mixture is heated so as to remove only the first organic solvent from the mixture. to thereby prepare a ceramic paste for forming a ceramic green layer 5 which compensates for spaces defined by step-like sections.

As described above, when the ceramic paste is prepared through at least two mixing steps. dispersibility of the ceramic powder is improved to some extent.

However, since the slurry or paste contains the organic binder. the viscosity of the slurry or paste becomes high during mixing. This imposes a limitation on improving dispersibility of the ceramic powder when an apparatus such as a ball mill is employed.

As already mentioned, there is a requirement for high dispersibility of the ceramic powder contained in the ceramic paste employed for forming the ceramic green layer 5 which compensates for spaces defined by step-like sections, the layer being very thin and having a thickness equal to that of the internal electrode 1. When the thickness of the internal electrode I decreases, the ceramic powder must exhibit a correspondingly higher dispersibility.

Even when dispersibility of the ceramic powder is low in the ceramic green layer 5, the ceramic green sheet 2 provided on the layer 5 may compensate for such low dispersibility to some extent. However, when the thickness of the sheet 2 decreases, the sheet cannot fully compensate for such low dispersibility.

Therefore, as the development of a monolithic ceramic capacitor of small size and large capacitance has progressed, there has been a growing need for high dispersibility of the ceramic powder contained in the ceramic green layer 5 which compensates for spaces defined by step-like sections.

In order to enhance dispersibility of the ceramic powder in the ceramic paste during mixing, the viscosity of the paste may be decreased. However, when the amount of the aforementioned organic solvent of low boiling point is increased in order to decrease the viscosity of the paste, removal of the solvent following

dispersion of the ceramic powder requires a prolonged perio d of time.

Hereinabove, problems to be solved are described with reference to a monolithic ceramic capacitor, but similar problems may be involved in other monolithic ceramic electronic components, such as a monolithic inductor.

## SUMMARY OF THE NVENTION

In view of the foregoing, an object of the present invention is to provide a process for producing a monolithic ceramic electronic component which enables solution of the above-described problems; and a monolithic ceramic electronic component produced through the process.

Another object of the present invention is to provide a process for producing a ceramic paste which is suitable for forming a very thin ceramic green layer such as the 6 above-described ceramic layer which compensates for spaces defined by step-like sections; and a ceramic paste which is produced through the process.

Accordingly, the present invention provides a process for producing a monolithic ceramic electronic component. The process comprises the following steps.

Firstly, a ceramic slurry, a conductive paste, and a ceramic paste are provided.

Subsequently. a plurality of composite structures are formed, each comprising a ceramic green sheet which is formed from the ceramic slurry; internal circuit element films which are formed by applying the conductive paste partially onto a main surface of the ceramic green sheet so as to provide step-like sections; and a ceramic green layer which compensates for spaces defined by the step-like sections, the ceramic green layer being formed by applying the ceramic paste to the region on the main surface of the ceramic green sheet on which the element films are not formed, so as to substantially compensate for the spaces.

Subsequently, the composite structures are laminated, to thereby form a green laminate.

Then, the green laminate is fired.

In the process for producing a monolithic ceramic electronic component comprising the above essential steps, a characteristic feature of the present invention resides in the step for providing the ceramic paste for formin g ceramic green layers; i.e., the process for producing the ceramic paste.

The production process for the ceramic paste comprises a first dispersion step in which a first mixture containing ceramic powder and a first organic solvent undergoes processing for providing a primary dispersion; and a second dispersion step in which a second mixture containing an organic binder and the first mixture which has undergone the first dispersion step undergoes processing for providing a secondary dispersion. It should be noted that the organic binder is added during the second dispersion step.

In the present invention, in addition to the first organic solvent, a second organic solvent having a relative evaporation rate lower than that of the first organic solvent is employed. The second organic solvent may be added during the first 7 dispersion step or the second dispersion step. Alternatively, the second organic solvent may be added during the first dispersion step, and further added during the second dispersion step. That is, the second organic solvent is contained in the first mixture and/or the second mixture.

After completion of the second dispersion step, the second mixture is heated, to thereby selectively remove the first organic solvent from the mixture.

In the first dispersion step of the process for producing the ceramic paste, the first mixture preferably contains an organic dispersant.

Preferably, the first organic solvent has a relative evaporation rate of 100 or more at 20'C, and the second organic solvent has a relative evaporation rate of 50 or less at 20'C.

In the production process for the ceramic paste, the second mixture is preferably subjected to filtration after completion of the second dispersion step and before the removal of the first organic solvent.

Preferably. the production process further comprises a step in which the organic binder is dissolved in the first organic solvent and/or the second organic solvent, to thereby form an organic vehicle, and a step in which the organic vehicle is subjected to filtration-, so that the second mixture contains the organic binder included in the organic vehicle which has been subjected to filtration.

In the production process, the first and second organic solvents are chosen such that the relative evaporation rate of the former is higher than that of the latter.

Usually, selection of these organic solvents is readily carried out when the first and second organic solvents are chosen such that the boiling point of the former is lower than that of the latter.

When the first and second organic solvents are chosen on the basis of the difference in the boiling points, the difference between the boiling point of the first organic solvent and that of the second organic solvent is preferably 50 degrees or more.

In the present invention, the ceramic slurry for forming the ceramic green sheet preferably contains ceramic powder having a composition substantially the same 9 as that of the ceramic powder contained in the ceramic paste for forming the ceramic green layer which compensates for spaces defined by step-like sections.

Preferably, dielectric ceramic powder is contained in a ceramic slurry and ceramic paste. In this case, when internal circuit element films are internal electrodes which are arranged so as to provide capacitance therebetween, a monolithic ceramic capacitor can be produced.

Preferably, magnetic ceramic powder is contained in a ceramic slurry and ceramic paste. In this case, when internal circuit element films are formed as hook shaped conductive films, a monolithic inductor can be produced.

The present invention also provides a monolithic ceramic electronic component produced through the above-described production process.

The present invention also provides a process for producing a ceramic paste as described above, and a ceramic paste produced through the process.

## BRIEF DESCRIPTION OF THE DRAWINGS

Various other objects, features, and many of the attendant advantages of the present invention will be readily appreciated as the same becomes better understood with reference to the following detailed description of the preferred embodiments when considered in connection with accompanying drawings, in which:

Fig- I is a schematic cross-sectional view of a portion of a green laminate 3a, illustrating a process for producing a monolithic ceramic capacitor of interest, which is an embodiment of the present invention; Fig. 2 is a plan view of a portion of a composite structure 6 which is produced through a production process for a monolithic ceramic capacitor as shown in Fig. 1; Fig. 3 is a schematic cross-sectional view of a lam1nate chip 4a which is produced through a production process for a monolithic ceramic capacitor as shown in Fig. 1; Fig. 4 is an exploded perspective view of elements constituting a green laminate 13 for producing a monolithic inductor, which is another embodiment of the present invention; 9 Fig. 5 is a perspective view of the appearance of a monolithic inductor I I containing a laminate chip 12 which is produced by firing the green laminate 13 shown in Fig. 4; Fig. 6 is a schematic cross-sectional view of a portion of a green laminate 3, illustrating a process for producing a conventional monolithic ceramic capacitor of interest; Fig. 7 is a plan view of a portion of a ceramic green sheet 2 on which internal electrodes I are formed through a production process for a monolithic ceramic capacitor as shown in Fig. 6; and Fig. 8 is a schematic cross-sectional view of a laminate chip 4 which is produced through a production process for a monolithic ceramic capacitor as shown in Fig. 6.

## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

One embodiment of the present invention will next be described by taking a production process for a monolithic ceramic capacitor as an example. The

production process will be described with reference to Figs. I through 3.

In order to carry out the embodiment, there are provided a ceramic slurry for forming a ceramic green sheet 2; a conductive paste for forming internal electrodes 1; and a ceramic paste for forming a ceramic green layer 5 which compensates for spaces defined by step-like sections formed by the electrodes 1.

The ceramic slurry is prepared by mixing dielectric ceramic powder, an organic binder, a plasticizer, and an organic solvent having a relatively low boiling point. The ceramic slurry is shaped into a sheet, by means of a doctor blade process or a similar process, on a support such as a polyester film (not shown in the Figs.) which is coated with a resin such as a silicone resin serving as a peeling agent, to thereby obtain the-ceramic green sheet 2. Subsequently, the resultant sheet is dried.

The thickness of the ceramic green sheet 2 is some Lni after drying.' On a main surface of the ceramic green sheet 2, the internal electrodes I are formed so as to be distributed at a plurality of positions. The thickness of each of the /0 electrodes is about 1 gm after firing. The internal electrodes 1 are formed. for example, by applying the conductive paste onto the ceramic green sheet 2 through screen printing, and then drying the paste. Each of the electrodes 1 has a predetermined thickness, and thus spaces defined by step-like sections formed by the electrodes 1 are provided on the ceramic green sheet 2.

Subsequently, the ceramic green layer 5 is formed on the region on the main surface of the ceramic green sheet 2 on which the internal electrodes 1 are not formed, so as to substantially compensate for the spaces defined by the step-like sections. The ceramic green layer 5 is formed by applying the ceramic paste onto the ceramic green sheet 2 through screen printing, so as to have a pattern negative to that of the internal electrodes 1. and then the resultant layer 5 is dried. The ceramic paste which is employed for forming the layer 5 has significant features in the present invention, and the paste will be described below in more detail.

In the above description, the ceramic green layer 5 is formed after the internal

electrodes 1 are formed. However, the ceramic green layer 5 may be formed before the internal electrodes 1 are formed.

A plurality of composite structures 6 are prepared. Each of the structures 6 as shown in Fig. 2 includes the ceramic green sheet 2. the internal electrodes 1, and the ceramic green layer 5, the electrodes and the layer being formed on the sheet as described above. Each of the composite structures 6 is peeled off the support, and then cut into appropriately sized pieces. Predetermined amounts of the pieces are laminated to form a lamination product, and then ceramic green sheets not containing such internal electrodes and ceramic green layers are laminated on opposite surfaces of the product, to thereby form a green laminate 3a as partially shown in Fig. 1.

The green laminate 3a is pressed in a vertical direction with respect to a horizontal plane., and then, as shown in Fig. 3, cut into appropriate] ysized laminate chips 4a such that-each of the chips can be suitably employed for producing a monolithic ceramic capacitor. Subsequently, the binder is removed-from the laminate chip, and the resultant chip is fired. Thereafter, external electrodes are formed on the chip. to thereby produce a monolithic ceramic capacitor.

As described above, when the ceramic green layer 5 is formed, in the green laminate 3a as partially shown in Fig. I, there is no substantial difference in thickness between the portion at which the electrodes I are provided and the portion at which the electrodes I are not provided; or the portion at which relatively large numbers of the internal electrodes I are provided in a vertical direction with respect to a horizontal plane and the portion at which small numbers of the electrodes are provided in a vertical direction with respect to a horizontal plane. Therefore, as shown in Fig. 3, the laminate chip 4a tends not to be undesirably deformed as it is in Fig. 8. Consequently, structural defects such as delamination or micro cracking, or short-circuiting may not occur in the resultant monolithic ceramic capacitor.

A characteristic feature of the present invention resides in the process for producing a ceramic paste for fon-ning the ceramic green layer 5. When the ceramic paste is produced through the process, dispersibility of the ceramic

powder contained in the paste can be enhanced.

In the present invention, in order to produce the ceramic paste, there are carried out a first dispersion step in which a first mixture containing ceramic powder and a first organic solvent is subjected to processing for providing a primary dispersion; and a second dispersion step in which a second mixture containing an organic binder and the first mixture which has been subjecte d to the first dispersion step is subjected to processing for providing a secondary dispersion.

In the first dispersion step, an organic binder is not added, and thus the first mixture can be subjected to processing for providing a primary dispersion at low viscosity. Therefore. dispersibility of the ceramic powder is easily enhanced. In the first dispersion step. air adsorbed on the ceramic powder is replaced by the first organic solvent, and thus the ceramic powder is sufficiently wetted with the first organic solvent, and the agglomerated ceramic powder is finely divided into particles as well.

In the second dispersion step, the organic binder can be mixed sufficiently and uniformly while dispersibility of the ceramic powder is maintained at a high level, the dispersibility being enhanced in the first dispersion step as described above. In M addition. the ceramic powder may further be pulverized in the second dispersion step.

In the present invention, in addition to the first organic solvent, a second organic solvent having a relative evaporation rate lower than that of the first organic solvent is employed. The second organic solvent may be added during the first dispersion step or the second dispersion step. Alternatively, the second organic solvent may be added during the first dispersion step, and further added during the second dispersion step.

After completion of the second dispersion step, the second mixture is heated, to thereby selectively remove the first organic solvent from the mixture.

As described above, the first organic solvent is removed after completion of the second dispersion step, and thus the viscosity of the second mixture can be maintained at a relatively low level during the second dispersion step. Therefore,

dispersibility can be maintained at a relatively high level, as well as the solubility of the organic binder, which is added during the second dispersion step as described above, can be enhanced.

The ceramic paste produced as described above substantially contains only the second organic solvent, although a trace amount of the first organic solvent may exist in the paste. Since the second organic solvent has a relative evaporation rate lower than that of the first organic solvent, the rate of drying of the ceramic paste can be reduced to a predetermined value or less. Therefore, the paste can be subjected to screen printing without any problem.

In the first and second dispersion steps of the production process, a customary apparatus such as a ball mill is employed for carrying out processing for providing a dispersion.

In the present invention, a variety of organic solvents may be employed as the first or second organic solvent. Therefore, an appropriate organic solvent may be chosen for each of the first and second organic solvents in consideration of the relative evaporation rate of the organic solvent.

Examples of such organic solvents include ketones such as methyl ethyl ketone, methyl isobutyl ketone. and acetone; hydrocarbons such as toluene, benzene, 13 xylene, and n-hexane. alcohols such as methanol, ethanol, isopropanol, butanol, and amyl alcohol; esters such as ethyl acetate, butyl acetate, and isobutyl acetate; ketones, esters, hydrocarbons, and alcohols; such as diisopropyl ketone, ethyl cellosolve, butyl cellosolve, cellosolve acetate, methyl cellosolve acetate, butyl carbitol, cyclohexanol, pine oil, dihydroterpineol, isophorone, terpineol, dipropylene glycol, and dimethyl phthalate; chlorinated hydrocarbons such as methylene chloride; and a mixture thereof.

In order to readily remove the first organic solvent after completion of the second dispersion step, the solvent preferably has a relative evaporation rate of 100 or more at 20'C, more preferably 150 or more. As used herein, the tenn "relative evaporation rate" refers to an evaporation rate relative to the evaporation rate of n butyl acetate (boiling point: 126.5'C) when the evaporation rate thereof is defined as 100. Relative evaporation rate is calculated on the basis of the

following formula:

Relative evaporation rate = (evaporation time of n-buty] acetate)/(evaporation time of subject solvent). wherein evaporation time is measured on the basis of weight.

Examples of organic solvents having a relative evaporation rate of 100 or more, which are suitable for the first organic solvent, include methyl ethyl ketone (relative evaporation rate: 465). methyl isobutyl ketone (relative evaporation rate:

145). acetone (relative evaporation rate: 720), toluene (relative evaporation rate: 195), benzene (relative evaporation rate: 500), methanol (relative evaporation rate: 370), ethanol (relative evaporation rate: 203), isopropanol (relative evaporation rate: 205), ethyl acetate(relative evaporation rate: 525), isobutyl acetate (relative evaporation rate: 152). butyl acetate (relative evaporation rate: 100), and a mixture thereof On the other hand, the second organic solvent preferably has a relative evaporation rate of 50 or less at 20'C, in order to allow efficient screen printing.

Examples of organic solvents having a relative evaporation rate of 50 or less, which are suitable for the second organic solvent, include diisopropyl ketone (relative evaporation rate: 49), methyl cellosolve acetate (relative evaporation rate: 40), cellosolve acetate (relative evaporation rate: 24), butyl cellosolve (relative evaporation rate: 10), cyclohexanol (relative evaporation rate: 10 or less), pine oil (relative evaporation rate: 10 or less). dihydroterpineol (relative evaporation rate: 10 or less), isophorone (relative evaporation rate: 10 or less), terpineol (relative evaporation rate:

or less). dipropylene glycol (relative evaporation rate: 10 or less), dimethyl phthalate (relative evaporation rate: 10 or less), butyl carbitol (relative evaporation rate: 40 or less), and a mixture thereof.

The first or second organic solvent may be chosen on the basis of its boiling point instead of its relative evaporation rate as described above. The first or second organic solvent is readily chosen on the basis of its boiling point rather

than its relative evaporation rate. In many cases, when the first and second organic solvents are chosen such that the boiling point of the former is lower than that of the latter. the relative evaporation rate of the former is higher than that of the latter.

Boiling points of some of the aforementioned organic solvents are as follows:

methyl ethyl ketone (79.6'C). methyl isobutyl ketone (1 18.O'C), acetone (56. 1 'C), toluene (11 LO'C). benzene (79.6'C), methanol (64.5'C), ethanol -(78.5'C), isopropanol (82.5'C). ethyl acetate (77. 1 'C), isobutyl acetate (1 18. PC), diisopropyl ketone (1 4').5'C), methyl cellosolve acetate (143'C), cellosolve acetate (1 56.2'C), butyl cellosolve (1 70.6'C). cyclohexanol (1 60'C). pine oil (1 95-225'C), dihydroterpineol (21 O'C), isophorone (215.2'C), terpineol (219.O'C), dipropylene glycol (23) 1.PC). and dimethyl phthalate (282.4'C). The first and second organic solvents may be chosen on the basis of such boiling points.

When the first and second organic solvents are chosen on the basis of the difference in the boiling points, the difference between the boiling point of the first oroanic solvent and that of the second organic solvent is preferably 50 degrees or more. This is because- when the difference is 50 degrees or more, the first organic solvent can be selectively and easily removed through heating after completion of the second dispersion step.

In order to facilitate screen printing, the second organic solvent preferably has a boiling point of 15WC or higher, more preferably about 200-250'C. When the boiling point is lower than 150'C, the ceramic paste dries rapidly, and thus the printing pattern meshes tend to be undesirably filled with the paste, whereas when the boiling point is higher than 2501C, the printed film is difficult to dry, and thus a prolonged period of time is necessary for drying.

The organic binder to be employed in the ceramic paste preferably dissolves in an organic solvent at room temperature. Examples of such an organic binder include polyacetals such as polyvinyl butyral and polybutyl butyral; poly(meth)acrylates; modified celluloses such as ethyl cellulose; alkyds; vinylidenes; polyethers; epoxy resins; urethane resins; polyamide resins; polyimide resins; polyamidoimide resins; polyester resins; polysulfone resins;

liquid crystal polymers; polyimidazole resins; and polyoxazoline resins.

The aforementioned polyvinyl butyral, serving as the organic binder, is produced through condensation between polyvinyl alcohol and butyraldehyde.

Polyvinyl butyral products include a low polymerization product, a medium polymerization product, and a high polymerization product, in which the amounts of an acetyl group and a butyral group are 6 mol% or less and 62-82-mol%, respectively.

The polyvinyl butyral product serving as the organic binder in the ceramic paste of the present invention is preferably a medium polymerization product in which the amount of a butyral group is about 65 mol%, in consideration of the viscosity of the polyvinyl butyral in an organic solution and the toughness of the film which is produced through drying of the polyvinyl butyral.

The amount of the organic binder is 1-20 wt.% on the basis of the entirety of the ceramic powder, preferably 3-10 wt.%.

In the first dispersion step, the first mixture preferably contains an organic dispersant. When an organic dispersant dissolved in the first organic solvent or in a mixture of the first and second solvents is added to the first mixture, dispersibility of the ceramic powder is further enhanced.

The type of organic dispersant employed is not particularly limited, but the dispersant preferably has a molecular weight of 10,000 or less in consideration of dispersibility thereof The dispersant may be an anionic dispersant, a cationic dispersant, or a nonionic dispersant. Examples of preferred dispersants include polyacrylic acids and ammonium salts thereof, polyacrylate copolymers, polyethylene /6 oxide, polyoxyethylene alkyl amyl ether, fatty acid diethanolamide, polyethylene imine, copolymers of polyoxypropylene monoallyl monobutyl ether and maleic anhydride (and styrene).

The amount of the organic dispersant is 0. 1-5 wt.%, preferably 0.5-2.0 wt.%, on the basis of the entirety of the ceramic powder.

The second mixture is preferably subjected to filtration after completion of the second dispersion step and before the first organic solvent is removed. Through filtration, impurities, flocculates of the ceramic powder, and non- dissolved organic binder, which may exist in the ceramic paste, can be removed, and thus dispersibility of the ceramic paste is reliably enhanced. In addition, very small air bubbles adhered to the ceramic powder are broken or removed through filtration, and thus, when the ceramic green layer 5 formed of the ceramic paste is fired, the amount of pinholes may be reduced in the resultant ceramic layer.

Alternatively, the organic binder is dissolved in the first organic solvent and/or the second organic solvent, to thereby form an organic vehicle; the organic vehicle is subjected to filtration; and the organic binder included in the vehicle which has been subjected to filtration may be added to the second mixture.

Each of the two types of filtration may be carried out repeatedly.

Alternatively, they may be carried out in combination. Whether filtration is carried out repeatedly or the two types of filtration are carried out in combination, dispersibility of the ceramic paste is further enhanced.

In the aforementioned filtration step, a filter formed from stainless steel or plastic such as polypropylene or fluorine-containing resin is employed. In order to increase filtration rate, the second mixture or the organic vehicle may be subjected to pressure using a gas such as air or nitrogen gas, or may be drawn through the filter by being subjected to reduced pressure.

The ceramic powder contained in the ceramic paste preferably has a composition substantially the same as that of the ceramic powder contained in the ceramic slurry for forming the ceramic green sheet 2. This is because, when these ceramic powders have substantially the same composition, the ceramic green layer 5 /7 and the ceramic green sheet 2 can be uniformly sintered.

When the ceramic powders have substantially the same composition, the powders contain the same primary component. For example, even when the powders contain different secondary components such as metallic oxide and glass in trace amounts, the powders are considered to have substantially the

same composition.

When the ceramic powder contained in the ceramic green sheet 2 satisfies temperature characteristics of capacitance; i.e., the B characteristic specified by JIS and the X7R characteristic specified by EIA, if the ceramic powder contained in the ceramic paste for forming the ceramic reen layer 5 has the same primary component and satisfies 9 1 the B and X7R characteristics, these powders are allowed to have different secondary components.

Fig. 4 illustrates the production process for a monolithic inductor which is another embodiment of the present invention. Fig. 5 is a perspective view of the appearance of a monolithic inductor I I Produced through the production process. Fig.

4 is an exploded perspective view of elements constituting a green laminate 13 for producing a laminated chip 12 contained in the monolithic inductor 11.

The green laminate 1-3 contains a plurality of ceramic green sheets 14, 15, 16, 17, 18, and 19, and is produced by laminating the sheets 14 through 19.

The ceramic green sheets 14 through 19 are produced by shaping a ceramic slurry containing magnetic ceramic powder into sheets by means of a doctor blade process or a similar process, and then drying the resultant sheets. Each of the ceramic green sheets 14 through 19 has a thickness, for example, of 10-30 Pin after drying.

On each of the sheets 15 through 18, which are located in the middle portion of the laminate L33. a hook-shaped conductive film and a ceramic green layer are formed which compensates for spaces defined by step-like sections formed by the film. A process for the formation of the film and the layer are described below.

Firstly, a hook-shaped conductive film 20 is formed on the ceramic green sheet 15. The film 20 -is formed such that a first end of the film extends to the edge of the sheet 15. A via hole conductor 21 is formed at a second end of the film 20.

A hole which is to be filled with the conductor 21 is formed in the sheet 15 by means of a laser or punching. Subsequently, the conductive paste is applied onto the sheet 15 through screen printing, and then the resultant sheet is dried, to thereby form the hook-shaped conductive film 20 and the via hole conductor 21.

A ceramic green layer 22 is formed on the region on the main surface of the ceramic green sheet 15 on which the hook-shaped conductive film 20 is not formed, so as to substantially compensate for spaces defined by the step-like sections formed by the film 20. The ceramic green layer 22 is formed by applying the ceramic paste onto the sheet 15 through screen printing, (the paste containing magnetic ceramic powder which has specific features in the present invention), and then drying the resultant sheet.

Subsequently. on the ceramic green sheet 16, a hook-shaped conductive film 23), a via hole conductor 24, and a ceramic green layer 25 which compensates for spaces defined by step-like sections formed by the film 23 are formed in a manner similar to that described above. A first end of the film 23 is connected to the second end of the film 20 with the intervention of the via hole conductor 2 1. The via hole conductor 24 is formed at a second end of the film 233.

Subsequently, on the ceramic green sheet 17, a hook-shaped conductive film 26, a via hole conductor 27, and a ceramic green layer 28 which compensates for spaces defined by step-like sections formed by the film 26 are formed in a manner similar to that described above. A first end of the film 26 is connected to the second end of the film 2-35 with the intervention of the via hole conductor 24. The via hole conductor 27 is formed at a second end of the film 26.

If necessary. the above-described lamination of the ceramic green sheets 16 and 17 is carried out repeatedly.

Subsequently. on the ceramic green sheet 18, a hook-shaped conductive film 29, and a ceramic -green layer 30 which compensates for spaces defined by step-like sections formed by the film 29 are formed. A first end of the film 29 is connected to the second end of the film 26 with the intervention of the via hole conductor 27. The film 29 is formed such that a second end thereof extends to

the edge of the sheet 18.

/9 Each of the hook-shaped conductive films 20, 23, 26, and 29 has a thickness of about _3 30 pm after drying.

In the green laminate 1 3), which is produced through the lamination of a plurality of composite structures including the ceramic green sheets 14 through 19, the hook-shaped conductive films 20, 23, 26, and 29 are successively connected to one another with the intervention of the via hole conductors 21, 24, and 27, to thereby form a coil-shaped conductor having a plurality of turns.

The laminate chip 12 which constitutes the monolithic inductor I I shown in Fig. 5 is produced by firing the green laminate 1-3). The green laminate U) shown in Fig. 4 is employed for producing only one laminate chip 12. However, a green laminate for producing a plurality of laminate chips may be formed. In this case, after the green laminate is formed, the laminate is cut into pieces, to thereby produce a plurality of laminate chips.

Subsequently. as shown in Fig. 5, external electrodes 30 and 31 are formed on the opposite ends of the laminate chip 12, such that the electrodes 30 and 31 are connected to the first end of the film 20 and the second end of the film 29, respectively, to thereby produce the monolithic inductor 11.

Ceramic powder is contained in the ceramic green sheet 2 and the ceramic green layer 5 which constitute the monolithic ceramic capacitor which is described above with reference to Figs. I through 3; and the ceramic powder is also contained in the ceramic green sheets 14 through 19 and the ceramic green layers 22, 25, 28, and )0 which constitute the monolithic inductor I I which is described above with reference to Figs. 4 and 5. Examples of the ceramic powder include ceramic powder of an oxide such as alumina, zirconia, magnesia, titanium oxide, barium titanate, lead titanate zirconate, or ferrite-manganese; and ceramic powder of a nonoxide such as silicon carbide. silicon nitride, or sialon. The ceramic powder which is employed is preferably pulveri-zed and has a spherical shape. The mean particle size of the powder is preferably 5 pm or less, more preferably I tm.

When barium titanate containing an alkali metal oxide as an impurity in an amount of 0. 1 wt.% or less is employed as the ceramic powder, a trace amount of the 2c following metallic oxide or glass component ma,,,. be incorporated into the ceramic powder.

Examples of the metallic oxide include terbium oxide, dysprosium oxide, holMium oxide, erbium oxide, ytterbium oxide, manganese oxide, cobalt oxide, nickel oxide, and magnesium oxide.

Examples of the glass component include Li.,-(SiTi)02-1V10(wherein MO refers to A1203 or Zr02), Si02-TiO2-MO (wherein MO refers to BaO, CaO, SrO, MgO, ZnO, or MnO), Li20-B203-(SiTi)02+MO (wherein MO refers to A1203 or Zr02), B.)03-Al203-MO (wherein MO refers to BaO. CaO. SrO, or MgO), and Si02.

A conductive paste is employed for forming the internal electrodes 1 which constitute the monolithic ceramic capacitor which 'Is described above with reference to Figs. 1 through 3); and the conductive paste is also employed for forming the hook shaped conductive films 20, 23), 26, and 29 and the via hole conductors 21, 24, and 27 which constitute the monolithic inductor 11 which is described above with reference to Figs. 4 and 5. The conductive paste employed will next be described.

The conductive paste employed in the monolithic ceramic capacitor includes copper powder, nickel powder, or conductive powder containing an alloy of Ag/Pd having a ratio of 60 wt.%/40 wt.% to 10 wi:%/90 Such powder has a mean particle size of 0.02-3) pm, preferably 0.05-0.5 pm. The powder (100 parts by weight); an organic binder (2-20 parts by weight, preferably 5-10 parts by weight); a resinate of a metal such as Ag, Au, Pt, Ti, Si, Ni, or Cu, serving as a sintering suppressing agent (about 0. 1 -3) parts by weight. preferably 0.5-1 parts by weight, as reduced to a metal); and an organic solvent (about 3 3 5 parts by weight) are kneaded by use of a three-roll mill. and then the same or a different organic solvent is further added to the resultant mixture to control the viscosity. to thereby prepare the conductive paste.

The conductive paste employed in the monolithic inductor 11 includes conductive powder containing Ag or an alloy of Ag/Pd having a ratio of 80

wt.%/20 wt.% to 100 wt.%/0 wt.%. The powder (100 parts by weight); and the organic binder, the sintering-suppressing agent, and the organic solvent. which are the same as those Q / employed in the above conductive paste. are kneaded at the same proportions as described above by use of a three-roll mill, and then the same or a different organic solvent is further added to the resultant mixture to control the viscosity, to thereby prepare the conductive paste.

EXAMPLES

The present invention will next be described in more detail by way of Test Examples.

(Test Example 1) Test Example I relates to a monolithic ceramic capacitor. Test Example I was carried out for confirming the effects of the first and second dispersion steps in the preparation of a ceramic paste for forming a ceramic green layer which compensates for spaces defined by step-like sections.

(Preparation of ceramic powder) Firstly, barium carbonate (BaC03) and titanium oxide (Ti02) were weighed so as to attain a mol ratio of 1: 1, and wet-mixed by use of a ball mill, and the resultant mixture was dehydrated and then dried. Subsequently the dried mixture was calcined at 1,000'C for two hours, and then pulverized, to thereby obtain dielectric ceramic powder.

(Preparation of ceramic slurry and formation of ceramic green sheet) The thus-prepared ceramic powder (100 parts by weight), polyvinyl butyral (medium polymerization product) (7 parts by weight), dioctyl phthalate (DOP) serving as a plasticizer (3 parts by weight), methyl ethyl ketone (30 parts by weight), ethanol (20 parts by weight), toluene (20 parts by weight), and zirconia grinding balls having a diameter of I mm (600 parts by weight) were placed in a ball mill, and wet-mixed for hours, to thereby prepare a ceramic slurry.

The resultant ceramic slurry was shaped into a ceramic green sheet having a thickness of 3 pm (2 pm after firing) by means of a doctor blade process. The sheet was dried at 801C for five minutes.

QR (Preparation of conductive paste) Metallic powder (Ag/Pd = 70/30) (100

parts by weight), ethyl cellulose (4 parts by weight), alkyd resin (2 parts by weight), Ag metallic resinate (3 parts by weight, 17.5 parts by weight as reduced to Ag), and butyl carbitol acetate (35 parts by weight) were kneaded by use of a three-roll mill, and then terpineol (35 parts by weight) was added to the resultant mixture to control the viscosity of the mixture.

(Preparation of ceramic paste for forming a ceramic green layer which compensates for spaces defined by step-like sections) Sample 1 The above-prepared dielectric ceramic powder (100 parts by weight), methyl ethyl ketone having a relative evaporation rate of 465 (70 parts by weight), and zirconia grinding balls having a diameter of 1 mm (600 parts by weight) were placed in a ball mill, and wet-mixed for 16 hours. Subsequently, terpineol having a boiling point of 220'C and a relative evaporation rate of 10 or less (40 parts by weight) and an ethyl cellulose resin (5 parts by weight) were added to the ball mill, and the resultant mixture was further mixed for 16 hours, to thereby obtain a ceramic slurry mixture.

Subsequently. the above-obtained ceramic slurry mixture was subjected to reduced-pressure distillation in a hot bath at WC by use of an evaporator for two hours. Through distillation, methyl ethyl ketone was completely removed from the slurry, to thereby obtain a ceramic paste. Then, terpineol (10 to 20 parts by weight) was added to the ceramic paste, and the resultant mixture was dispersed in an automatic mortar, to thereby regulate the viscosity of the mixture.

Sample 2 The above-prepared dielectric ceramic powder (100 parts by weight). methyl ethyl ketone (70 parts by weight), terpineol (30 parts by weight), and zirconia grinding balls having a diameter of 1 mm (600 parts by weight) were placed in a ball mill. and wet-mixed for 16 hours. Subsequently, terpineol having a boiling point of 22CC (10 parts by weight) and an ethyl cellulose resin (5 parts by weight) were added to the ball mill, and the resultant mixture was further mixed for 16 hours, to thereby obtain a ceramic slurry mixture.

23 Subsequently. the above-obtained ceramic slurry mixture was subjected to reduced-pressure distillation in a hot bath at WC by use of an evaporator for two hours. Through distillation, methyl ethyl ketone was completely removed from

the slurry, to thereby obtain a ceramic paste. Then, terpineol (10 to 20 parts by weight) was added to the ceramic paste, and the resultant mixture was dispersed in an automatic mortar. to thereby control the viscosity of the mixture.

Sample 3 3 The above-prepared dielectric ceramic powder (100 parts by weight), methyl ethyl ketone (70 parts by weight), a polyacrylic acid quaternary ammonium salt dispersant (weight average molecular weight: 1,000) (0.5 parts by weight), and zirconia grinding balls having a diameter of 1 mm (600 parts by weight) were placed in a ball mill, and wet-mixed for 16 hours. Subsequently, terpineol having a boiling point of 220'C (10 parts by weight) and an ethyl cellulose resin (5 parts by weight) were added to the ball mill, and the resultant mixture was further-mixed for 16 hours, to thereby obtain a ceramic slurry mixture.

Subsequently, the above-obtained ceramic slurry mixture was subjected to reduced-pressure distillation in a hot bath at WC by use of an evaporator for two hours. Through distillation, methyl ethyl ketone was completely removed from the slurry, to thereby obtain a ceramic paste. Then, terpineol (10 to 20 parts by weight) was added to the ceramic paste, and the resultant mixture was dispersed in an automatic mortar, to thereby control the viscosity of the mixture.

Sample 4 The above-prepared dielectric ceramic powder (100 parts by weight), terpineol having a boiling point of 220'C (40 parts by weight). and an ethyl cellulose resin (5 parts by weight) were mixed in an automatic mortar, and then kneaded by use of a three-roll mill, to thereby obtain a ceramic paste.

(Productidn of monolithic ceramic capacitor) The conductive paste was applied onto a main surface of the above-forined ceramic green sheet through screen printing, and then dried at WC for 10 minutes, to thereby form internal electrodes. The size, shape, and position of the internal electrodes were determined so as to fit a laminate chip produced in the below described step. Subsequently, the ceramic paste of each of Samples 1 through, applied onto the main surface of the ceramic green sheet through screen printin then dried at WC for 10 minutes, to thereby form a ceramic green layer which compensates for spaces defined by step-like sections. The thicknesses of the inte electrode and the ceramic green layer were 1 pm after drying and 0.5 gm after firil

Subsequently, the ceramic green sheets containing the internal electrodes ai the ceramic green layer (200 sheets) were laminated, and then the lamination produ'(', was sandwiched by some tens of ceramic green sheets not containing internal electrodes, to thereby form a green laminate. The green laminate was thermally 2 pressed at WC under a pressure of 1,000 Kg/em Subsequently. the resultant laminate was cut into a plurality of laminate chips by use of a cutting blade. The dimensions of each of the chips were determined so as to attain dimensions of,' 3.2 min (length) x 1.6 mm (width) x 1.6 mm (thickness) after firing.

Subsequently, the above-obtained laminate chips were arranged on a setter for firing on which a small amount of zirconia powder had been distributed, and the temperature of the chips was elevated from room temperature to 250'C over 24 hours, to thereby remove the organic binder. Then, the resultant chips were placed in a firing furnace, and the chips were fired with a temperature profile having a maximum temperature of 1,300'C for about 20 hours.

Next. each of the resultant sintered chips was placed in a barrel, and then the side surfaces of the chip were sujected to polishing. Thereafter, external electrodes were formed on the opposite sides of the sintered chip, to thereby produce a monolithic ceramic capacitor as a sample.

(Evaluatiob of characteristics) The ceramic paste and the monolithic ceramic capacitor of each of Samples 1 through 4 were evaluated for a variety of characteristics. The results are shown in Table 1.

(Table 1) (1) Sample No.

(2) Solid content (wt.%) (3) Viscosity (Pa-s) (4) Dispersion degree (5) Thickness of printed film (tm) (6) Ra (tm) (7) Ratio of structural defects (%) The characteristics shown in Table I were evaluated as follows.

Solid content: the ceramic paste (about I g) was weighed accurately, and then the paste was allowed to stand in a heat convection-type oven at 150'C for three hours. The solid content of the paste was calculated on the basis of the weight of the paste after heating.

Viscosity: the viscosity of the ceramic paste was measured by use of an Etype viscometer (product of Tokyo Keiki) at 20'C at a revolution number of 2.5 rpm.

Dispersion degree: the particle size distribution of the ceramic powder was measured by use of a light diffraction particle size distribution measuring apparatus, and the degree of dispersion of the powder was calculated on the basis of the resultant data. Briefly, the above-prepared ceramic powder was dispersed in water by use of an ultrasonic homogenizer, and the particles were subjected to ultrasonic waves until they were reduced to their minimum size. When the particles reached their minimum size, the particle size at D90 of the particle size distribution was recorded as "limitation particle size." Separately, the ceramic paste was diluted with ethanol, and the particle size at D90 of the particle size distribution was recorded as "paste particle size." The dispersion degreeof the ceramic powder was calculated on the basis of the following formula:

dispersion degree = (paste particle size/limitation particle size) - 1. In the case in which the dispersion degree assumes a positive value, when the value is nearer to Q6 zero, dispersibility of the powder is high. In contrast, in the case in which the dispersion degree assumes a negative value, when the larger the absolute value, the higher the dispersibility of the powder.

Thickness of printed film: the ceramic paste was applied onto a 96% alumina substrate so as to attain a thickness of 20 Lrn by use of a 400-mesh stainless steel screen having a thickness of 50 trn, and the resultant substrate was dried at 800C for minutes, to thereby form a printed film for evaluation. The thickness of the film was obtained using the data as measured by a non-contact-type laser surface roughness meter.

Surface roughness (Ra): a printed film for evaluation was formed in a manner similar to that described above. The surface roughness (Ra) of the film; i.e., the averaged absolute value of deviation of a undulation-averaged center line and a roughness curve, was obtained from the data measured by a non-contact- type laser surface roughness meter.

Ratio of structural defects: the resultant sintered chip for producing a monolithic ceramic capacitor was observed by appearance and under an ultrasonic microscope. When some unusual portions were observed, the internal structural defects of the chip was confirmed after the chip had been polished. The ratio of structural defects was obtained on the basis of the following relation: (the number of sintered chips having structural defects/the total number of sintered chips).

As is apparent from Table 1, the ceramic pastes and the capacitors of Samples I through 3-in which the first and second dispersion steps were carried out, and the organic binder was added during the second dispersionstep----exhibit excellent characteristics in terms of dispersibility, thickness of printed film, surface roughness, and ratio of structural defects, as compared with the ceramic paste and the capacitor of Sample 4, in which such procedures were not carried out.

(Test Example 2) Test Example 2 also relates to a monolithic ceramic capacitor. Test Example 2 was carried out to confirm the effects of addition of the filtration step in the preparation of a ceramic paste for forming a ceramic green layer which compensates for spaces defined by step-like sections.

The procedure of Test Example 1 was repeated, except that the step of 44preparation of ceramic paste for forming a ceramic green layer which compensates for spaces defined by step-like sections" was carried out as described below, to thereby produce monolithic ceramic capacitors.

(Preparation of ceramic paste for forming a ceramic green layer which compensates for spaces defined by step-like sections) Sample 5 A ceramic slurry mixture which was prepared in a manner similar to the case of Sample 1 of Test Example 1 was subjected to filtration under pressure through use of a filter having an absolute filtration precision of 20 pm (i.e., a substance having a size of 10 pm or more can be removed through the filter at a probability of 99.7%).

Subsequently, the resultant ceramic slurry mixture was subjected to processing in a manner similar to the case of Sample 1 of Test Example 1, to-thereby obtain a ceramic paste.

Sample 6 The preparation procedure for Sample 5 was repeated, except that, after completion of filtration through use of a filter having an absolute filtration precision of 20 pm, filtration through use of a filter having an absolute filtration precision of 1 pm was further carried out under pressure, to thereby obtain a ceramic paste.

Sample 7 Terpineol having a boiling point of 22WC (40 parts by weight), methyl ethyl ketone (10 parts by weight). and an ethyl cellulose resin (5 parts by weight) were mixed with a planetary mixer, to thereby prepare an organic vehicle. Subsequently, the organic vehicle was subjected to filtration under pressure through use of a filter having an absolute filtration precision of 20 pm.

Separately, the above-prepared dielectric ceramic powder (100 parts by weight), methyl ethyl ketone (60 parts by weight), and zirconia grinding balls having a diameter of 1 mm (600 parts by weight) were placed in a ball mill, and wet-mixed for 16 hours.

9 Subsequently,.. the above-prepared organic vehicle which had been subjected to filtration was added to the ball mill, and the resultant mixture was further mixed for 16 hours, to thereby obtain a ceramic slurry mixture.

The ceramic slurry mixture was subjected to processing in a manner similar to the case of Sample 1 of Test Example 1, to thereby obtain a ceramic paste.

Sample 8 The preparation procedure for Sample 7 was repeated, except that, after completion of filtration through use of a filter having an absolute filtration precision of 20 pm, filtration through use of a filter having an absolute filtration precision of 1 im was further carried out under pressure, to thereby obtain a ceramic paste.

Sample 9 The preparation procedure for Sample 7 was repeated, and filtration of the ceramic slurry mixture was further carried out in a manner similar to the case of Sample 5. to thereby obtain a ceramic paste.

The ceramic paste and the monolithic ceramic capacitor of each of Samples 5

through 9 were evaluated in terms of a variety of characteristics. The results are shown in Table 2.

(Table 2) (1) Sample No.

(2) Solid content (wt.%) (3) Viscosity (Pa.s) (4) Dispersion degree (5) Thickness of printed film (ptm) (6) Ra (kim) (7) Ratio of structural defects The methods for evaluating the characteristics shown in Table 2 are similar to those employed for the items shown in Table 1.

Sample 5 shown in Table 2 is different from Sample 1 shown in Table 1 in that the ceramic slurry mixture of Sample 5 was subjected to filtration. Therefore, Q9 comparison between Sample 5 and Sample 1 reveals the effect of filtration. That is, the comparison reveals that the ceramic paste and the capacitor of Sample 5 exhibit excellent characteristics in terms of dispersibility, thickness of printed film, surface roughness, and ratio of structural defects, as compared with the ceramic paste and the capacitor of Sample 1.

As shown in Table 2, comparison between Samples 5 and 6; comparison between Samples 7 and 8; comparison between Samples 5 and 9; and comparison between Samples 7 and 9 reveal that, when filtration is carried out repeatedly or different types of filtration are carried out in combination. the effects are further enhanced.

(Test Example 3) Test Example 3 also relates to a monolithic ceramic capacitor. Test Example 33 was carried out to confirm the preferable relative evaporation rate range for each of the first and second organic solvents employed in the production of a ceramic paste for forming a ceramic green layer which compensates for spaces defined by step-like sections.

The procedure of Test Example 1 was repeated. except that the step of "preparation of ceramic paste for forming a ceramic green layer which compensates for spaces defined by step-like sections" was carried out as described below, to thereby produce monolithic ceramic capacitors.

1 (Preparation of ceramic paste for forming a ceramic green layer which

compens ates for spaces defined by step-like sections) Sample 10 The preparation procedure for Sample 1 of Test Example 1 was repeated, except that n-butyl acetate having a relative evaporation rate of 100 was employed as a first organic solvent, to thereby prepare a ceramic paste.

Sample 11 The preparation procedure for Sample 1 of Test Example 1 was repeated, except that acetone having a relative evaporation rate of 720 was employed as a first organic solvent, to thereby prepare a ceramic paste.

Sample 12 The preparation procedure for Sample 1 of Test Example 1 was repeated, except that isobutyl alcohol having a relative evaporation rate of 83 was employed as a first organic solvent, to thereby prepare a ceramic paste.

Sample 1 3 3 The preparation procedure for Sample 1 of Test Example 1 was repeated, except that methanol having a relative evaporation rate of 370 was employed as a first organic solvent, and that methyl cellosolve having a relative evaporation rate of 55 was employed as a second organic solvent, to thereby prepare a ceramic paste.

The ceramic paste and the monolithic ceramic capacitor of each of Samples 10 through 1 J3) were evaluated in terms of a variety of characteristics. The results are shown in Table -33. Table -3) also shows the first and second organic solvents employed in Samples 10 through 1 3 3.

(Table (1) Sample No:

(2) First organic solvent (relative evaporation rate) (3)) Second organic solvent (relative evaporation rate) (4) Evaporation time (Hr) (5) Solid content (wt.%) (6) Viscosity (Pa-s) (7) Dispersion degree (8) Ra (pm) (9) Ratio of structural defects (%) (10) n-Butyl acetate (100) (11) Acetone (720) (12) Isobutyl alcohol (83) (131.) Methanol (370) (14) Terpineol (10 or less) (15) Methyl cellosolve (55) (16) Evaporation continues for a long period of time 3/ In Table 33. the heading "evaporation time" refers to the time from the beginning of evaporation under reduced pressure to the end of evaporation of the organic solvent (usually the first organic solvent). The methods for evaluating the characteristics shown in Table 3 other than the "evaporation time" are similar to those employed for the

items in Table 1.

As is apparent from Table 3, in Samples 10 and 11, evaporation of the first organic solvent is completed within a short period of time, since the first organic solvent has a relative evaporation rate of 100 or more and the second organic solvent has a relative evaporation rate of 50 or less. In addition, the ceramic pastes and the capacitors of Samples 10 and I I exhibit excellent characteristics in terms of dispersibility. surface roughness, and ratio of structural defects.

In contrast, in Sample 12, evaporation of the first organic solvent is not completed within a short period of time, since the first organic solvent has a relative evaporation rate of less than 100, although the second organic solvent has a relative evaporation rate of 50 or less. The ceramic paste and the capacitor of Sample 12 exhibit poor characteristics in terms of dispersibility, surface roughness, and ratio of structural defects, as compared with those of Samples 10 and 11.

Evaporation of the second organic solvent continued for a long period of time in Sample 13, since the second organic solvent has a relative evaporation rate of more than 50, although the first organic solvent has a relative evaporation rate of 100 or more. In this case, the ceramic paste dries rapidly during screen printing, and thus screen meshes are undesirably filled with the paste, resulting in poor screen printing.

(Test Example 4) Test Example 4 relates to a monolithic inductor. Test Example 4 was carried out to confirm the effects of the first and second dispersion steps in the preparation of a ceramic paste for forming a ceramic green layer which compensates for spaces defined by step-like sections.

(Preparation of ceramic powder) Ferric oxide powder, zinc oxide powder, nickel oxide powder, and copper oxide powder were weighed so as to attain proportions of 49.0 mol%, 29.0 mol%, 3Q 14.0 niol%, and 8.0 mol%, respectively. These po¥ ders were wet-mixed by use of a ball mill, and the resultant mixture was dehydrated to dryness. Subsequently the dried mixture was calcined at 75WC for one hour, and then pulverized, to thereby obtain magnetic ceramic powder.

(Preparation of ceramic slurry and formation of ceramic green sheet) The thus-prepared magnetic ceramic powder (100 parts by weight), polyvinyl butyral (medium polymerization product) (7 parts by weight), dioctyl phthalate (DOP) serving as a plasticizer (3) parts by weight), methyl ethyl ketone (30 parts by weight), ethanol (20 parts by weight), toluene (20 parts by. weight). and zirconia grinding balls having a diameter of 1 mm (600 parts by weight) were placed in a ball mill, and wet mixed for 20 hours, to thereby prepare a ceramic slurry.

The resultant ceramic slurry was shaped into a ceramic green sheet having a thickness of 20 Vim (15 Vim after firing) by means of a doctor blade process. The sheet was dried at WC for five minutes.

(Preparation of conductive paste) Metallic powder (Ag/Pd = 70/30) (100 parts by weight), ethyl cellulose (4 parts by weight), alkyd resin (2 parts by weight). Ag metallic resinate (3 parts by weight, 17.5 parts by weight as reduced to Ag), and butyl carbitol acetate (35 parts by weight) were kneaded by use of a three-roll mill, and then terpineol (35 parts by weight) was added to the resultant mixture to control the viscosity of the mixture.

(Preparation of ceramic paste for forming a ceramic green layer which compensates for spaces defined by step-like sections) Sample 14 - The above-prepared magnetic ceramic powder (100 parts by weight), methyl ethyl ketone having a relative evaporation rate of 465 (70 parts by weight), and zirconia grinding balls having a diameter of 1 mm (600 parts by weight) were placed in a ball mill, andwet-mixed for 16 hours. Subsequently. terpineol having a boiling point of 220C and a relative evaporation rate of 10 or less (40 parts by weight) and an ethyl cellulose resin (5 parts by weight) were added to the ball mill, and the resultant mixture was further mixed for 16 hours, to thereby obtain a ceramic slurry mixture.

33 Subsequently, the above-obtained ceramic slurry mixture was subjected to reduced-pressure distillation in a hot bath at WC by use of an evaporator for two hours. Through distillation, methyl ethyl ketone was completely removed from the slurry, to thereby obtain a ceramic paste. Then, terpineol (10 to 20 parts by weight) was added to the ceramic paste, and the resultant mixture was

dispersed in an automatic mortar, to thereby control the viscosity of the mixture.

Sample 15 The above-prepared magnetic ceramic powder (100 parts by weight), methyl ethyl ketone (70 parts by weight), terpineol (30 parts by weight), and zirconia grinding balls having a diameter of 1 mm (600 parts by weight) were placed in a ball mill, and wet-mixed for 16 hours. Subsequently, terpineol having a boiling point of 22WC (10 parts by weight) and an ethyl cellulose resin (5 parts by weight) were added to the ball mill, and the resultant mixture was further mixed for 16 hours, to thereby obtain a ceramic slurry mixture.

Subsequently, the above-obtained ceramic slurry mixture was subjected to reduced-pressure distillation in a hot bath at WC by use of an evaporator for two hours. Through distillation, methyl ethyl ketone was completely removed from the slurry, to thereby obtain a ceramic paste. Then, terpineol (10 to 20 parts by weight) was added to the ceramic paste, and the resultant mixture was dispersed in an automatic mortar, to thereby control the viscosity of the mixture.

Sample 16 The above-prepared magnetic ceramic powder (100 parts by weight), methyl ethyl ketone (70 parts by weight), a polyacrylic acid quaternary ammonium salt dispersant (weight average molecular weight: 1,000) (0.5 parts by weight), and zirconia grinding balls having a diameter of 1 mm (600 parts by weight) were placed in a ball mill, and wet-mixed for 16 hours. Subsequently, terpineol having a boiling point of 22CC (10 parts by weight) and an ethyl cellulose resin (5 parts by weight) were added to the ball mill, and the resultant mixture was further mixed for 16 hours, to thereby obtain a ceramic slurry mixture.

3//- Subsequently, the above-obtained ceramic slurry mixture was subjected to reduced-pressure distillation in a hot bath at 60'C by use of an evaporator for two hours. Through distillation, methyl ethyl ketone was completely removed from the slurry, to thereby obtain a ceramic paste. Then, terpineol (10 to 20 parts by weight) was added to the ceramic paste, and the resultant mixture was dispersed in an automatic mortar, to thereby control the viscosity of the mixture.

Sample 17 The above-prepared magnetic ceramic powder (100 parts by weight), terpineol having a boiling point of 220'C (40 parts by weight), and an ethyl

cellulose resin (5 LI parts by weight) were mixed in an automatic mortar, and then kneaded by use of a three-roll mill, to thereby obtain a ceramic paste.

(Production of monolithic inductor) A hole to be filled a via hole conductor was formed in a predeten-nined position of the above-prepared magnetic ceramic green sheet such that a coil-shaped conductor was able to be fori-ned after a plurality of the sheets were laminated.

Separately. a conductive paste was applied to the magnetic ceramic green sheet, and then dried at 80'C for 10 minutes, to thereby form a hook-shaped conductive film on the main surface of the sheet and a via hole conductor in the hole. Subsequently, each of the magnetic ceramic pastes of Sample 14 through 17 was applied onto the magnetic ceramic green sheet, and then dried at 80'C for 10 minutes, to thereby form a magnetic ceramic green layer which compensates for spaces defined by step-like sections. The thicknesses of the hook-shaped conductive film and the ceramic green layer were _330 pm after drying and 20 im after firing.

Subsequently, the magnetic ceramic green sheets containing the hookshaped conductive film, the via hole conductor, and the ceramic green layer (I I sheets) were laminated, such that a coil-shaped conductor was formed inside the resultant lamination product. Thereafter, the lamination product was sandwiched by magnetic ceramic green sheets not containing the hook-shaped conductive films, to thereby form a green laminate. The green laminate was thermally pressed at 80'C under a 2 pressure of 1,000 Kg/cm Subsequently. the resultant laminate was cut into a plurality of laminate chips by use of a cutting blade. The dimensions of each of the chips were determined so as to attain dimensions of 3.2 mm (length) x 1.6 mm (width) x 1.6 mm (thickness) after firing.

Subsequently, the laminate chip was heated at 400'C for two hours, to thereby remove the organic binder, and then the resultant chip was fired at 900'C for 90 minutes.

Next, the resultant slntered chip was placed in a barrel, and then the side surfaces of the chip were subjected to polishing. Thereafter, external electrodes predominantly formed of silver were formed on the opposite sides of the sintered

chip, to thereby produce a chip-type monolithic inductor as a sample.

(Evaluation of characteristics) The ceramic paste and the monolithic inductor of each of Samples 14 through 17 were evaluated in terms of a variety.of characteristics. The results are shown in Table 4.

(Table 4) (1) Sample No.

(2) Solid content (wt.%) (3)) Viscosity (Pa-s) (4) Dispersion degree (5) Thickness of printed film (tm) (6) Ra (pm) (7) Ratio of structural defects The methods for evaluating the characteristics shown in Table 4 are similar to those employed for the items shown in Table 1.

As is apparent from Table 4, the ceramic pastes and the capacitors of Samples 14 through 16-in which the first and second dispersion steps were carried out, and the organic binder was added during the second dispersion step---exhibit excellent characteristics in terms of dispersibility, thickness of printed film, surface roughness, 36 and ratio of structural defects. as compared with the ceramic paste and the capacitor of Sample 17 in which such procedures were not carried out. The results are similar to those-of Test Example I shown in Table 1.

Hereinabove, the case in which dielectric ceramic powder or magnetic ceramic powder i, s incorporated into the ceramic paste of the present invention is described.

However, in the present invention, the characteristics of the ceramic paste are not influenced by electric characteristics of the ceramic powder contained in the paste.

Therefore. the ceramic paste containing insulating ceramic powder or piezoelectric ceramic powder exhibits characteristics similar to those of the ceramic paste containing dielectric ceramic powder or magnetic ceramic powder.

Z__ As described above, according to the present invention, a ceramic paste is

produced through the following steps: a first dispersion step in which a first mixture containing ceramic powder and a first organic solvent undergoes processing for providing a primary dispersion, a second dispersion step in which a second mixture containing an organic binder and the first mixture which has undergone the first dispersion step undergoes processing for providing a secondary dispersion; a step in which a second organic solvent having a relative evaporation rate lower than that of the first organic solvent is added to the first mixture and/or the second mixture; and a removal step for selectively removing the first organic solvent from the second mixture through heating the second mixture. Consequently, dispersibility of the ceramic powder contained in the ceramic paste can be further enhanced. Therefore, the ceramic paste is advantageously employed for forining a very thin ceramic green layer at high pattern accuracy.

According to the present invention, since a ceramic paste is employed for forming a ceramic green layer on the region on the main surface of a ceramic green sheet on which internal circuit element films are not formed, so as to substantially compensate for spaces defined by the step-like sections formed by the films, the resultant monolithic ceramic electronic component does not have structural defects such as cracking and delamination, and exhibits high reliability.

-37 According to the present invention, the size and the weight of a monolithic ceramic electronic component can be satisfactorily reduced. Therefore, when the present invention is applied to a monolithic ceramic capacitor, the size of the capacitor can be advantageously reduced and the capacitance thereof can be advantageously increased. In addition, when the present invention is applied to a monolithic inductor, the size of the inductor can be advantageously reduced and the inductance thereof can be advantageously increased.

When an organic dispersant is incorporated into the first mixture during the above-described first dispersion step, dispersibility of the ceramic powder is further enhanced.

When the first organic solvent has a relative evaporation rate of 100 or more at 20'C and the second organic solvent has a relative evaporation rate of 50 or less

at 20'C, the first organic solvent can be readily removed during the removal step, and in addition, screen printing is facilitated.

When the second mixture is subjected to filtration after completion of the second dispersion step and before the removal step; or when the organic binder is dissolved in the first organic solvent and/or the second organic solvent to thereby form an organic vehicle, the organic vehicle is subjected to filtration, and then added to the second mixture, impurities, flocculates of the ceramic powder, and non- dissolved organic binder, which may exist in the ceramic paste, can be removed, and thus dispersibility of the ceramic paste is reliably enhanced. In addition, the amount of pinholes may be reduced in the resultant ceramic layer.

The first and second organic solvents are chosen such that the relative evaporation rate of the former is higher than that of the latter. Thus, when the first and second organic solvents are chosen such that the boiling point of the former is lower than that of the latter, these solvents are readily chosen.

In the cast in which the first and second organic solvents are chosen on the basis of the difference in the boiling point, when the difference between the boiling point of the first organic solvent and that of the second organic solvent is 50 degrees or more, the first organic solvent can be selectively and easily removed through 33 heating after completion of the second dispersion step.

In the process for producing a monolithic ceramic electronic component of the present invention, a ceramic green sheet and a ceramic green layer which compensates for spaces defined by step-like sections can be uniformly sintered when ceramic powder contained in a ceramic slurry for forming the ceramic green sheet has a composition substantially the same as that of ceramic powder contained in a ceramic paste for forming the ceramic green layer. When the ceramic green sheet and the ceramic green layer are uniformly sintered, cracking or delamination can be prevented.

Table 1.

Sample No 1 2 3 4 Solid content (wt.%) 65 64 66 67 Viscosity (Pas) 9 8 10 12 Dipersion degree 0 0 -0.2 0.3 Thickness of printed film(pm) 4 4 3 5 R6 (pm) 0.5 1

0.5 1 0.3 1.5 Ratio of structural defects 2 3 0 80 1.0 Table 2.

Sample No 5 6 7 8 9 Solid content (wt.%) 66 67 66 67 68 Viscosity (Pa.s) 10 12 15 14 16 Dispersion degree -0.1 -0.2 0 0 -0.3 Thickness of printed film(pm) 3 2 3 2 2 RA (pm) 0.4 0.3 0.5 0.5 0.2 Ratio of structural defects 1.5 1 1.5 1 0 Table 3.

Sample No. 10 11 12 13 First organic solvent n-Butyle acetate Acetone Isobutyle alcohol Methanol (relative evaporation rate) (100) (720) (83) (370) Second organic solvent Terpineol Terpineol Terpineol Methyl cellosolve (relative evaporation rate) (10 or less) (10 or less) (10 or less) (55) Evaporation continues Evaporation time (Hr) 2 1 4 for a long period of time Solid content (wt.%) 70 67 66 Viscosity (Pa.s) 15 9 10 Dispersion degree 0.2 0 0.4 R6 (pm) 0.7 0.5 1.0 Ratio of structural defects %) 3 2 Table 4.

Sample No 14 15 16 17 Solid content (wt.%) 72 73 72 73 Viscosity (Pa.s) 15 14 17 18 Dispersion degree 0 0 -0.3 0.2 Thickness of printed film(pm) 20 21 19 19 R (pm) 0.5 0.5 0.2 1 1.6 Ratio of structural defects 1 1 0 50

CLAIMS:

1. A process for producing a monolithic ceramic electronic component, which comprises:

providing a ceramic slurry, a conductive paste, and a ceramic paste; forming a plurality of composite structures each comprising a ceramic green sheet produced by shaping the ceramic slurry, internal circuit element films formed by applying the conductive paste partially onto a main surface of the ceramic green sheet so as to provide step-like sections, and a ceramic green layer which compensates for spaces defined by the step-like sections, the ceramic green layer being formed by applying the ceramic paste onto the region on the main surface of the sheet on which the element films are not formed, so as to substantially compensate for the spaces; forming a green laminate by laminating the composite structures; and firing the green laminate. wherein a process for providing- the ceramic paste comprises:

a first dispersion step in which a first mixture containing ceramic powder and a first organic solvent undergoes processing for providing a primary dispersion; a second dispersion step in which a second mixture containing an organic binder and the first mixture which has

undergone the first dispersion step undergoes processing for providing a secondary dispersion; a step in which a second organic solvent having a relative evaporation rate lower than that of the first organic solvent is incorporated into the first mixture and/or the second mixture; and a removal step for selectively removing the first organic solvent from the second mixture through heating the second mixture.

2. A process for producing a monolithic ceramic electronic component according to claini 1. wherein the first mixture comprises an organic dispersant during the first dispersion step.

3 ). A process for producing a monolithic ceramic electronic component according to clairn 1 or 2. wherein the first organic solvent has a relative evaporation 41 rate of' 100 or more and at 20'C, and the second organic solvent has a relative evaporation rate of 50 or less at 20'C.

4. A process for producing a monolithic ceramic electronic component according to any one of claims I through 3, wherein the process for providing the ceramic paste further comprises a step in which the second mixture undergoes filtration after the second dispersion step and before the removal step.

5. A process for producing a monolithic ceramic electronic component according to any one of claims I through 4, wherein the process for providing the ceramic paste further comprises a step in which the organic binder is dissolved in the first organic solvent and/or the second organic solvent to thereby form an organic vehicle; and a step in which the organic vehicle undergoes filtration, and the second mixture comprises the organic binder included in the organic vehicle which has undergone filtration.

6. A process for producing a monolithic ceramic electronic component according to any one of claims I through 5, wherein the first organic solvent has a boiling point lower than that of the second organic solvent.

7. A process for producing a monolithic ceramic electronic component according to claim 6. wherein difference between the boiling point of the first organic solvent and that of the second organic solvent is 50 degrees or more.

8. A process for producing a monolithic ceramic electronic component according to any one of claims I through 7, wherein the ceramic slurry comprises ceramic powder which has a composition substantially the same as that of the ceramic powder contained in the ceramic

paste.

9. A process for producing a monolithic ceramic electronic component according to any one of claims I through 8, wherein the ceramic powder contained in each of the cerarnic slurry and the ceramic paste is dielectric ceramic powder.

10. A process for producing a monolithic ceramic electronic component according to claim 9, wherein the internal circuit element films are internal electrodes which are arranged so as to provide capacitance therebetween, and the monolithic ceramic electronic component is a monolithic ceramic capacitor.

11. A process for producing a monolithic ceramic electronic component according to any one of claims I through 8, wherein the ceramic powder contained in each of the ceramic slurry and the ceramic paste is magnetic ceramic powder.

12. A process for producing a monolithic ceramic electronic component according to claim 11, wherein the internal circuit element films are hook-shaped conductive films, and the monolithic ceramic electronic component is a monolithic inductor.

13. A monolithic ceramic electronic component which is produced through a process as recited in any one of claims I through 12.

14. A process for producing a ceramic paste, which comprises:

a first dispersion step in which a first mixture containing ceramic powder and a first organic solvent undergoes processing for providing a primary dispersion; a second dispersion step in which a second mixture containing an organic binder and the first mixture which has undergone the first dispersion step undergoes processing for providing a secondary dispersion; a step in which a second organic solvent having a relative evaporation rate lower than that of the first organic solvent is incorporated into the first mixture and/or the second mixture; and a removal step for selectively removing the first organic solvent from the second mixture through heating the second mixture.

15. A ceramic paste which is produced through a process as recited in claim 14.

16. A process for producing a monolithic electric capacitor as herein before described with

reference to the accompanying drawings.

17. A monolithic capacitor as herein before described with reference to the accompanying drawings.

18. A process for producing a ceramic paste as herein before described with reference to the accompanying drawings.

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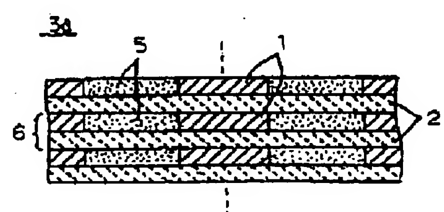
[54]发明名称 单块陶瓷电子元件及其制造方法和陶瓷糊浆及其制造方法

[57]摘要

单块陶瓷电子元件的制造方法，包括提供陶瓷淤浆、导电胶和陶瓷糊浆；形成多个复合结构，各自包括陶瓷淤浆形成的陶瓷坯料片，导电胶在该片材表面上形成的阶梯状内线路元件薄膜，用于补偿该阶梯状区域造成的空隙的陶瓷坯料层，该层是将陶瓷糊浆涂在坯料片表面上无元件薄膜区域制得的，从而基本补偿所述空隙；将复合结构叠合成叠合物坯料；以及烧制该叠合物坯料。还提供该方法制得的单块陶瓷电子元件，陶瓷糊浆和陶瓷糊浆的制造方法。

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# 说　　明　　书

## 单块陶瓷电子元件及其制造方法和陶瓷糊浆及其制造方法

本发明涉及一种单块陶瓷电子元件及其制造方法，并涉及陶瓷糊浆及其制造方法。更具体地说，本发明涉及的单块陶瓷电子元件包括形成于陶瓷片材之间的内线路元件薄膜，以及用于补偿由内线路元件薄膜形成的阶梯状区域造成的空隙的陶瓷层，形成的各陶瓷层使之形状与相应的薄膜相反；涉及这种电子元件的制造方法；并涉及能有利地形成所述陶瓷层的陶瓷糊浆及其制造方法。

当制造单块陶瓷电子元件(如单块陶瓷电容器)时，先形成多块陶瓷坯料片，随后叠合这些坯料片。根据单块陶瓷电子元件所需的性能，在具体的陶瓷坯料片上形成内线路元件薄膜(如导电薄膜或电阻薄膜)，该薄膜可作为电容、电阻、电感、变阻器、滤波器等的元件。

近年来对电子设备(如移动通讯设备)进行小型化并降低重量。例如，当将单块陶瓷电子元件作为电路元件用于这种电子设备中时，必须降低这种电子元件的大小和重量。例如，需要小尺寸和大容量的单块陶瓷电容器。

制备单块陶瓷电容器的具体方法如下：将介电陶瓷粉末、有机粘合剂、增塑剂和有机溶剂混合在一起制得陶瓷淤浆。用刮刀法或类似的方法在支承垫(如聚酯膜，它涂覆硅氧烷树脂作为剥离试剂)上将得到的陶瓷淤浆制成数十微米厚的片材，形成陶瓷坯料片。随后干燥该坯料片。

接着，用网印法在陶瓷坯料片的主表面上施涂导电胶，形成相互隔开的多种图案。随后干燥形成的片材，形成在片材上作为内线路元件薄膜的内电极。图 7 是陶瓷坯料片 2 部分的平面图，其上面形成有内电极 1，如上所述该内电极分布在多个位置。

随后从支承垫上剥离陶瓷坯料片 2，将其切割成合适的大小。随后部分如图 6 所示将预定量的多片坯料叠合在一起。另外，将预定量的不含内电极的陶瓷坯料片叠合在形成的叠合物的相反表面上，形成层叠物坯料 3。

沿相对于水平面垂直方向压制该层叠物坯料 3，随后如图 8 所示将其切割成层叠的晶片 4，该晶片具有合适的尺寸，能用作单独的单块陶瓷电容器。接着从各晶片除去粘合剂，烧制形成的晶片，随后在晶片上形成外电极，从而制得单块陶瓷电容器。

为了减小这种电容器的尺寸并提高其电容量，必须增加叠合的陶瓷坯料片 2 和内电极 1 的数量，同时必须降低陶瓷坯料片 2 的厚度。

但是，当如上所述增加叠合的坯料片和内电极的数量并降低坯料片的厚度时，内电极 1 会积聚起来(accumulate)。结果，有内电极 1 的部分和无内电极 1 的部分(或者沿相对水平面的垂直方向具有相对大量内电极 1 的部分与沿垂直方向较少具有内电极 1 的部分)之间的厚度差异明显。因此，例如如图 8 所示，形成的叠合晶片 4 的外形变形，其主表面呈突起状。

当叠合的晶片 4 如图 8 所示变形时，在压制过程中在无内电极 1 的部分或者沿与水平面垂直方向电极 1 的量相对较少的部分会产生相对大的应变。另外，陶瓷坯料片 2 之间的粘性下降，并且会产生结构缺陷(如脱层或微开裂)，这种缺陷是烧制过程中晶片内部应力造成的。

当叠合晶片 4 如图 8 所示变形时，内电极 1 也会不合需求地变形，从而会导致短路。

上述问题会降低形成的单块陶瓷电容器的可靠性。

为了解决上述问题，例如日本未审定公开专利 56-94719、3-74820 和 9-1069025 公开了一种方法，如图 2 所示它在陶瓷坯料片 2 的无内电极 1 的区域形成陶瓷坯料层 5，从而基本补偿由陶瓷坯料片 2 上的内电极 1 造成的阶梯状区域形成的空隙。

如上所述，在形成用于补偿阶梯状区域造成的空隙的陶瓷坯料层 5 的情况下，当形成如图 1 部分所示的层叠物坯料 3a 时，在有电极 1 的区域和无电极 1 的区域之间，或者在沿相对水平面的垂直方向有相对大量的内电极 1 的区域和沿垂直方向有相对少量电极 1 的区域之间的厚度差异不明显。因此，如图 3 所示，形成的叠合晶片 4a 不会如图 8 所示那样发生不合需求的变形。

结果，不会发生上述结构缺陷(如脱层或微开裂)或者由于内电极 1 的变形导致的短路，从而提高形成的单块陶瓷电容器的可靠性。

上述用于补偿阶梯状区域造成的空隙的陶瓷坯料层 5 的组成与陶瓷坯料片 2 的组成相同，坯料层 5 是将含有介电陶瓷粉末、有机粘合剂、增塑剂和有机溶剂的陶瓷糊浆涂覆在坯料层 2 上制得的。为了通过网印高精度地制得层 5 使之厚度(例如 2 微米或更小)与内电极 1 的厚度相等，陶瓷粉末必须在陶瓷糊浆中具有高的分散性。

对于上述文献，例如日本未审定专利申请 No. 3-74820 公开了一种陶瓷糊浆的制造方法，其中使用三辊研磨机分散陶瓷粉末。但是，仅使用三辊研磨机难以

提高陶瓷粉末的分散性。

日本未审定专利申请 No. 9-106925 公开了用于形成陶瓷坯料片 2 的陶瓷淤浆是通过混合介电陶瓷粉末、有机粘合剂和具有低沸点的第一有机溶剂而制得的，并将形成的淤浆用于制造陶瓷坯料片 2；将该淤浆与沸点高于第一有机溶剂沸点的第二有机溶剂相混合，并加热形成的混合物以仅从混合物中除去第一有机溶剂，制得的陶瓷糊浆用于形成陶瓷坯料层 5 以补偿阶梯状区域造成的空隙。

如上所述，当至少通过两个混合步骤制得陶瓷糊浆时，在某种程度上改进了陶瓷粉末的分散性。但是，由于糊浆或淤浆含有有机粘合剂，因此在混合过程中糊浆或淤浆的粘度变高。当使用例如球磨设备时，粘度上升限制了分散性的改进。

如前面已提到的那样，要求用于形成用来补偿阶梯状区域造成的空隙的陶瓷坯料层 5(该层非常薄，厚度等于内电极 1 的厚度)的陶瓷糊浆中所含的陶瓷粉末具有高的分散性。当降低内电极 1 的厚度时，陶瓷粉末必须表现出相应更高的分散性。

即使在陶瓷坯料层 5 中陶瓷粉末的分散性较小，在该层 5 上的陶瓷坯料片 2 也会在某种程度上补偿这种低的分散性。但是，当片材 2 的厚度降低时，该片不能完全补偿这种低的分散性。

因此，随着小尺寸大容量的单块陶瓷电容器的发展，要求用于补偿阶梯状区域造成的空隙的陶瓷坯料层中所含的陶瓷粉末具有高的分散性。

为了在混合过程中提高陶瓷粉末在陶瓷糊浆中的分散性，可降低糊浆的粘度。但是，当增加上述低沸点有机溶剂的量以降低糊浆的粘度时，在分散陶瓷粉末后需要更长时间来除去溶剂。

上面参照单块陶瓷电容器描述了要解决的问题，但是相同的问题也包括在其它单块陶瓷电子元件中，例如单块电感器中。

由于上述问题，因此本发明的一个目的是提供一种能解决上述问题的单块陶瓷电子元件的制造方法，以及用这种方法制得的单块陶瓷电子元件。

本发明另一个目的是提供一种陶瓷糊浆的制造方法，该陶瓷糊浆适合形成很薄的陶瓷坯料层(例如上述用于补偿阶梯状区域造成的空隙的陶瓷层)，以及用这种方法制得的陶瓷糊浆。

因此，本发明提供一种单块陶瓷电子元件的制造方法。该方法包括下列步骤：

首先，提供陶瓷淤浆、导电胶和陶瓷糊浆；

接着，形成多个复合结构；各个结构包括由所述陶瓷淤浆制成的陶瓷坯料片，由将所述导电胶局部施涂在陶瓷坯料片主表面上形成的内线路元件薄膜，从而造成阶梯状区域，以及用于补偿该阶梯状区域造成的空隙的陶瓷坯料层，所述陶瓷坯料层是将陶瓷糊浆施涂在陶瓷坯料片主表面上未形成元件薄膜的区域而制得的，从而基本补偿所述空隙；

最后，将复合结构叠合在一起形成叠合物坯料。

随后烧制该叠合物坯料。

在由上述基本步骤组成的单块陶瓷电子元件的制造方法中，本发明的特征在于提供陶瓷糊浆以形成陶瓷坯料层的步骤，即制造陶瓷糊浆的方法。

陶瓷糊浆的制造方法包括第一分散步骤，该步骤对含有陶瓷粉末和第一有机溶剂的第一混合物进行初次分散；以及第二分散步骤，该步骤对含有有机粘合剂和经第一分散步骤处理的第一混合物的第二混合物进行二次分散。应注意有机粘合剂是在第二分散步骤过程中加入的。

在本发明中，除了第一有机溶剂以外，还使用相对蒸发速率低于第一有机溶剂的相对蒸发速率的第二有机溶剂。第二有机溶剂可在第一分散步骤过程中或第二分散步骤过程中加入。或者，第二有机溶剂可在第一分散步骤过程中加入，并在第二分散步骤过程中进一步加入。也就是说，第二有机溶剂包含在第一混合物和/或第二混合物中。

在第二分散步骤完成后，加热第二混合物，从该混合物中选择性地除去第一有机溶剂。

在陶瓷糊浆制造方法的第一分散步骤中，第一混合物较好含有有机分散剂。

第一有机溶剂的相对蒸发速率较好在 20℃为 100 或更高，第二有机溶剂的相对蒸发速率在 20℃为 50 或更低。

在陶瓷糊浆的制造方法中，在第二分散步骤完成后并在除去第一有机溶剂之前较好对第二混合物进行过滤。

所述制造方法较好还包括将有机粘合剂溶解在第一有机溶剂和/或第二有机溶剂中从而形成有机载体的步骤，以及对该有机载体进行过滤的步骤，从而使第二混合物含有经过滤的在有机载体中的有机粘合剂。

在所述制造方法中，选择第一和第二有机溶剂使得第一有机溶剂的相对蒸发速率高于第二有机溶剂的相对蒸发速率。通常，选用第一和第二有机溶剂使得第一有机溶剂的沸点低于第二有机溶剂的沸点，就可容易地选择这些有机溶剂。

当基于不同的沸点选择第一和第二有机溶剂时，第一有机溶剂的沸点和第二

有机溶剂的沸点较好相差50°或更多。

在本发明中，用于形成陶瓷坯料片的陶瓷淤浆所含的陶瓷粉末的组成较好与形成用于补偿阶梯状区域形成的空隙的陶瓷坯料层的陶瓷糊浆所含的陶瓷粉末的组成相同。

较好的是，在陶瓷淤浆和陶瓷糊浆中含有介电陶瓷粉末。在这种情况下，当内线路元件薄膜排列成相互间能形成电容的内电极时，可制得单块陶瓷电容器。

较好的是，在陶瓷淤浆和陶瓷糊浆中含有磁性陶瓷粉末。在这种情况下，当内线路元件薄膜形成钩状导电薄膜时，可制得单块电感器。

本发明还提供用上述方法制得的单块陶瓷电子元件。

本发明还提供如上所述的陶瓷糊浆的制造方法，和用该方法制得的陶瓷糊浆。

下面参照附图的详细描述可更好地理解本发明的其它目的、特征和许多附加优点。附图中

图 1 是本发明一个实例的部分叠合物坯料 3a 的剖面图，说明感兴趣的单块陶瓷电容器的制造方法；

图 2 是复合结构 6 部分的平面图，该结构是用图 1 所示的单块陶瓷电容器的制造方法制得的；

图 3 是叠合晶片 4a 的平面图，它是用图 1 所示的单块陶瓷电容器的制造方法制得的；

图 4 是本发明另一个实例中，构成用于制造单块电感器的叠合物坯料 13 的元件分解透视图；

图 5 是含有叠合基片 12 的单块电感器 11 的外观透视图，该单块电感器是通过烧制图 4 所示的叠合物坯料 13 而制得的；

图 6 是部分叠合物坯料 3 的剖面图，说明感兴趣的常规单块陶瓷电容器的制造方法；

图 7 是部分陶瓷坯料片 2 的平面图，在该坯料片上通过图 6 所示的单块陶瓷电容器的制造方法形成内电极 1；以及

图 8 叠合晶片 4 的剖面图，它是用图 6 所示的单块陶瓷电容器的制造方法制得的。

下面以单块陶瓷电容器的制造方法为例说明本发明的一个实例。该制造方法将参照图 1 至图 3 进行描述。

为了实施本实例，提供用于形成陶瓷坯料片 2 的陶瓷淤浆，用于形成内电极

1 的导电胶，和形成用于补偿构成电极 1 的阶梯状区域形成的空隙的陶瓷坯料层 5 的陶瓷糊浆。

陶瓷淤浆是将介电陶瓷粉末、有机粘合剂、增塑剂和沸点相对较低的有机溶剂混合在一起而制得的。使用刮刀法或相似的方法使陶瓷淤浆在支承垫(如聚酯膜，图中未表示)上形成片材，该支承垫涂覆有树脂(如硅氧烷树脂)作为剥离试剂，从而得到陶瓷坯料片 2。随后，干燥该片材，干燥后陶瓷坯料片 2 的厚度为数微米。

在陶瓷坯料片 2 的一个主表面上形成内电极 1，使之分布在多个位置。烧制后该电极的厚度约为 1 微米。内电极 1 是例如将导电胶网印施涂在陶瓷坯料片 2 上，随后干燥该导电胶而形成的。各个内电极 1 均具有预定的厚度，从而在陶瓷坯料片 2 上形成由内电极 1 构成的阶梯状区域造成的空隙。

接着，在陶瓷坯料片 2 的该主表面的未形成内电极 1 的区域形成陶瓷坯料层 5，以便基本补偿由所述阶梯状区域造成的空隙。陶瓷坯料层 5 是将陶瓷糊浆网印在陶瓷坯料片 2 上形成的，使其图案与内电极 1 相反，随后干燥形成的层 5。本发明用于形成层 5 的陶瓷糊浆具有很大的优点，该糊浆将在下面详细描述。

在上面描述中，陶瓷坯料层 5 是在内电极 1 形成后制得的。但是，该陶瓷坯料层也可在内电极 1 形成前制得。

制备多个复合结构 6。如图 2 所示各个复合结构 6 包括陶瓷坯料片 2、内电极 1 和陶瓷坯料层 5，电极和坯料层是如上所述形成在坯料片上的。从支承垫上剥离各个复合结构 6，随后切割成合适大小的片。将预定量的片叠合成叠合产物，接着在该产物的相反两个表面叠合不含这种内电极和陶瓷坯料层的陶瓷坯料片，从而形成部分如图 1 所示的叠合物坯料 3a。

沿与水平面垂直的方向压制叠合坯料 3a，随后如图 3 所示将其切割成适当大小的叠合晶片 4a，使得每块晶片均适用于制造单块陶瓷电容器。接着，从叠合晶片上除去粘合剂，并烧制形成的晶片。随后在晶片上形成外电极制得单块陶瓷电容器。

如上所述，在形成陶瓷坯料层 5 后，在部分如图 1 所示的叠合物坯料 3a 中具有电极 1 的区域和不具有电极 1 区域(或者在沿与水平面垂直方向具有相对大量内电极 1 的区域和沿与水平面垂直的方向具有少量电极的区域)之间的厚度无明显差异。因此，如图 3 所示，叠合晶片 4a 不会如图 8 所示的那样不合需求地发生变形。结果，在形成的单块陶瓷电容器中不会发生结构缺陷，如脱层或微开裂或者短路。

本发明的特征在于用于形成陶瓷坯料层5的陶瓷糊浆的制造方法。当用本方法制造陶瓷糊浆时，可提高该糊浆中所含陶瓷粉末的分散性。

在本发明中，为了制造陶瓷糊浆，进行第一分散步骤和第二分散步骤，在第一分散步骤中对含有陶瓷粉末和第一有机溶剂的第一混合物进行初次分散，在第二分散步骤中对含有有机粘合剂和经过第一分散步骤处理的第一混合物的第二混合物进行二次分散。

在第一分散步骤中，不加入有机粘合剂，因此可在低粘度下对第一混合物进行初次分散，从而可容易地提高陶瓷粉末的分散性。在第一分散步骤中，吸附在陶瓷粉末上的空气被第一有机溶剂所取代，从而用第一有机溶剂完全湿润陶瓷粉末，并且团聚的陶瓷粉末也被细分成颗粒。

在第二分散步骤中，可充分混合有机粘合剂并使之均匀，同时使陶瓷粉末的分散性保持在高的水准，如上所述在第一分散步骤中该分散性得到强化。另外，在第二分散步骤中可进一步粉碎该陶瓷粉末。

在本发明中，除了第一有机溶剂以外，使用相对蒸发速率低于第一有机溶剂的相对蒸发速率的第二有机溶剂。第二有机溶剂可在第一分散步骤过程中或在第二分散步骤过程中加入。或者，可在第一分散步骤过程中加入第二有机溶剂，并在第二分散步骤过程中进一步加入该溶剂。

在第二分散步骤完成后，加热第二混合物，从该混合物中选择性地除去第一有机溶剂。

如上所述，在完成第二分散步骤后除去第一有机溶剂，从而在第二分散步骤过程中使第二混合物的粘度保持在相对较低的水准。因此，分散性可保持在相对高的水准，并且可增强如上所述在第二分散步骤过程中加入的有机粘合剂的溶解度。

如上所述制得的陶瓷糊浆基本仅含第二有机溶剂，尽管在糊浆中会存在痕量第一有机溶剂。由于第二有机溶剂的相对蒸发速率低于第一有机溶剂的相对蒸发速率，因此可使陶瓷糊浆的干燥速率下降至预定的值或更小。因此，可网印该糊浆而不会产生问题。

在本制造方法的第一和第二分散步骤中，使用常规的设备(如球磨机)来实施分散步骤。

在本发明中，可使用各种有机溶剂作为第一或第二有机溶剂。因此，在有机溶剂相对蒸发速率的基础上选择合适的有机溶剂作为第一有机溶剂和第二有机溶剂。

这种有机溶剂的例子包括酮，如甲乙酮、甲基异丁基酮和丙酮；烃，如甲苯、苯、二甲苯和正己烷；醇，如甲醇、乙醇、异丙醇、丁醇和戊醇；酯，如乙酸乙酯、乙酸丁酯和乙酸异丁酯；酮、酯、烃和醇，如二异丙基酮、乙基溶纤剂、丁基溶纤剂、乙酸溶纤剂、乙酸甲基溶纤剂、丁基卡必醇、环己醇、松油、二氢萜品醇、异佛尔酮、萜品醇、二丙二醇和邻苯二甲酸甲二醇酯；氯化烃，如二氯甲烷及其混合物。

在完成第二分散步骤后，为能容易地除去第一有机溶剂，该溶剂在20℃的相对蒸发速率为100或更大为佳，更好的为150或更大。本文中，术语“相对蒸发速率”指将乙酸正丁酯(沸点：126.5℃)的蒸发速率定义为100时，相对于乙酸正丁酯的蒸发速率。相对蒸发速率按下列公式计算：

相对蒸发速率=(乙酸正丁酯的蒸发时间)/(所述溶剂的蒸发时间)，其中所述蒸发时间是单位重量的蒸发时间。

相对蒸发速率为100或更大，适合作为第一溶剂的有机溶剂的例子包括甲基乙基酮(相对蒸发速率：465)、甲基异丁基酮(相对蒸发速率：145)、丙酮(相对蒸发速率：720)、甲苯(相对蒸发速率：195)、苯(相对蒸发速率：500)、甲醇(相对蒸发速率：370)、乙醇(相对蒸发速率：203)、异丙醇(相对蒸发速率：205)、乙酸乙酯(相对蒸发速率：525)、乙酸异丁酯(相对蒸发速率：152)、乙酸丁酯(相对蒸发速率：100)、或它们的混合物。

另一方面，第二有机溶剂在20℃时的相对蒸发速率宜为50或更小，以足以进行网印。

相对蒸发速率为50或更小，适合作为第二有机溶剂的有机溶剂的例子包括二异丙基酮(相对蒸发速率：49)、乙酸甲基溶纤剂(相对蒸发速率：40)、乙酸溶纤剂(相对蒸发速率：24)、丁基溶纤剂(相对蒸发速率：10)、环己醇(相对蒸发速率：10或更小)、松油(相对蒸发速率：10或更小)、二氢萜品醇(相对蒸发速率：10或更小)、异佛尔酮(相对蒸发速率：10或更小)、萜品醇(相对蒸发速率：10或更小)、二丙二醇(相对蒸发速率：10或更小)、邻苯二甲酸甲二醇酯(相对蒸发速率：10或更小)、丁基卡必醇 (相对蒸发速率：40或更小)、或它们的混合物。

可用沸点代替上述相对蒸发速率来选择第一或第二有机溶剂。根据沸点而非相对蒸发速率可容易地选择第一或第二有机溶剂。在许多情况下，当选择第一和第二有机溶剂，使前者的沸点低于后者的沸点时，前者的蒸发速率大于后者的蒸发速率。

前面所述的一些有机溶剂的沸点如下：甲基乙基酮(79.6℃)、甲基异丁基酮

(118.0℃)、丙酮(56.1℃)、甲苯(111.0℃)、苯(79.6℃)、甲醇(64.5℃)、乙醇(78.5℃)、异丙醇(82.5℃)、乙酸乙酯(77.1℃)、乙酸异丁酯(118.3℃)、二异丙基酮(143.5℃)、乙酸甲基溶纤剂(143℃)、乙酸溶纤剂(156.2℃)、丁基溶纤剂(170.6℃)、环己醇(160℃)、松油(195-225℃)、二氢萜品醇(210℃)、异佛尔酮(215.2℃)、萜品醇(219.0℃)、二丙二醇(231.8℃)、邻苯二甲酸二甲酯(282.4℃)。可根据上面的沸点选择第一和第二有机溶剂。

当根据沸点差异选择第一和第二有机溶剂时，第一和第二有机溶剂的沸点差宜为 50℃或更大。这是因为当沸点差为 50℃或更大时，可以在完成第二分散步骤后，通过加热容易地选择性除去第一有机溶剂。

为实施网印，较好的第二有机溶剂沸点为 150℃或更高，约 200－250℃更好。当沸点低于 150℃时，陶瓷糊浆迅速干燥，带图案的印网会不合需求地填充糊浆，而当沸点高于 250℃时，印刷膜难以干燥，延长了干燥所需的时间。

用于陶瓷糊浆的有机粘合剂较好在室温溶解于有机溶剂中，这种有机粘合剂的例子包括聚缩醛，如聚乙烯醇缩丁醛和聚丁醇缩丁醛；聚(甲基)丙烯酸酯；改性纤维素，如乙基纤维素；醇酸树脂；亚乙烯基树脂(vinylidenes)；聚醚；环氧树脂；聚氨酯树脂；聚酰胺树脂；聚酰亚胺树脂；聚酰氨基酰亚胺树脂；聚酯树脂；聚砜树脂；液晶聚合物；聚咪唑树脂和聚噁唑啉树脂。

上述作为有机粘合剂的聚乙烯醇缩丁醛是聚乙烯醇和缩丁醛缩合而成的。聚乙烯醇缩丁醛产物包括低聚合产物、中度聚合产物和高聚合产物，其中的乙酰基和缩丁醛基的量分别为 6 摩尔％或更低和 62-82 摩尔％。考虑到有机溶液中聚乙烯醇缩丁醛的粘度和聚乙烯醇缩丁醛干燥后制得的薄膜的韧度，在本发明陶瓷糊浆中作为有机粘合剂的聚乙烯醇缩丁醛产物较好是中度聚合产物，其中缩丁醛基团的含量约为 65 摩尔％。

按陶瓷粉末的总量计，有机粘合剂的含量为 1-20 重量％，较好为 3-10 重量％。

在第一分散步骤中，第一混合物较好含有有机分散剂。当将溶解在第一有机溶剂中或者在第一和第二有机溶剂的混合物中的有机分散剂加入第一混合物中时，可进一步提高陶瓷粉末的分散性。

所使用的有机分散剂的类型无特别限制，但是考虑到其分散性，分散剂的分子量较好为 10,000 或更低。该分散剂可以是阴离子分散剂、阳离子分散剂或非离子分散剂。较好的分散剂的例子包括聚丙烯酸及其铵盐、聚丙烯酸酯共聚物、聚环氧乙烷、聚氧乙烯烷基戊基醚、脂肪酸二乙醇酰胺、聚乙烯亚胺、聚氧化丙烯

单烯丙基单丁基醚和马来酸酐(和苯乙烯)的共聚物。

按陶瓷粉末的总量计，有机分散剂的含量为 0.1-5 重量%，较好为 0.5-2.0 重量%。

在完成第二分散步骤并且在除去第一有机溶剂前最好对第二混合物进行过滤。通过过滤，可除去陶瓷糊浆中可能存在的杂质、陶瓷粉末絮凝物和不溶解的有机粘合剂。从而可可靠地提高陶瓷糊浆的分散性。另外，过滤可打碎或除去粘附在陶瓷粉末上的很小的气泡，从而在由陶瓷糊浆形成的陶瓷坯料层 5 烧制后，可减少形成的陶瓷层中的针孔。

或者，将有机粘合剂溶解在第一有机溶剂和/或第二有机溶剂中，形成有机载体，对该有机载体进行过滤，再将包含在经过滤的有机载体中的有机粘合剂加至第二混合物中。

可重复进行这两种过滤步骤。或者，可组合这些过滤步骤。无论是重复过滤还是组合进行这两种过滤步骤，均可进一步提高陶瓷糊浆的分散性。

在上述过滤步骤中，可使用不锈钢或塑料(如聚丙烯或含氟树脂)形成的过滤器。为了提高过滤速度，可使用气体(如空气或氮气)对第二混合物或有机载体进行加压，或者通过减压对过滤器进行抽滤。

陶瓷糊浆中所含的陶瓷粉末的组成较好与用于制造陶瓷坯料片 2 的陶瓷淤浆所含的陶瓷粉末的组成基本相同。这是因为当这些陶瓷粉末具有基本相同的组成时，陶瓷坯料层 5 和陶瓷坯料片 2 可以均匀地烧结。

当这二种陶瓷粉末具有基本相同的组成时，这些粉末含有相同的主要组分。例如，即使粉末含有痕量不同的次要组分如金属氧化物和玻璃时，仍可认为该粉末具有基本相同的组成。当陶瓷坯料片 2 所含的陶瓷粉满足电容器的温度特性(即 JIS 规定的 B 特性和 EIA 规定的 X7R 特性)时，如果用于制造陶瓷坯料层 5 的陶瓷糊浆中包含的陶瓷粉末具有相同的主要组分，并且满足 B 和 X7R 特性，则允许这些粉末包含不同的次要组分。

图 4 说明本发明另一个实例的单块电感器的制造方法。图 5 是用该制造方法制得的单块电感器 11 的外观透视图。图 4 是构成制备单块电感器 11 中的叠合晶片 12 的叠合物坯料 13 的各部件的分解透视图。

叠合物坯料 13 包含多个陶瓷坯料片 14、15、16、17、18 和 19，它是将片 14－19 叠合在一起制得的。

陶瓷坯料片 14－19 是用刮刀法或类似的方法，将包含磁性陶瓷粉末的陶瓷淤浆成形为片材，然后干燥而制得的。干燥后陶瓷坯料片 14－19 的厚度各为例

如 10—30 微米。

在位于层叠物 13 中部的各片片材 15—18 上形成有钩形的导电膜和陶瓷坯料层，该陶瓷坯料层用于补偿由所述导电膜形成的阶梯状区域造成的空隙。下面描述制备该导电膜和陶瓷层的方法。

首先，在陶瓷坯料片 15 上形成钩形导电膜 20。形成导电膜 20 使其第一端伸至陶瓷片 15 的边缘。在膜 20 的第二端形成一通孔导体 21。

采用激光或穿孔，在陶瓷坯料片 15 上形成用于填入导体 21 的孔。随后，通过网印在陶瓷坯料片 15 上涂布导电胶，然后干燥得到的片材，形成钩形导电膜 20 和通孔导体 21。

在陶瓷坯料片 15 的主表面上没有形成钩形导电膜 20 的区域形成陶瓷坯料层 22，使之基本补偿由膜 20 形成的阶梯状区域造成的空隙。陶瓷坯料层 22 是将陶瓷糊浆(该糊浆含有磁性陶瓷粉末，具有本发明的特征)网印在陶瓷坯料片 15 上而形成的，随后干燥形成的片材。

随后，在陶瓷坯料片 16 上，按照与上述相同的方式形成钩形导电膜 23，通孔导体 24 和用于补偿由膜 23 的阶梯状区域造成的空隙的陶瓷坯料层 25。膜 23 的第一端通过插入的通孔导体 21 与膜 20 的第二端相连。在膜 23 的第二端形成通孔导体 24。

之后，在陶瓷坯料片 17 上，按照与上述相同的方式形成钩形导电膜 26、通孔导体 27 和用于补偿由膜 26 的阶梯状区域造成的空隙的陶瓷坯料层 28。膜 26 的第一端通过插入的通孔导体 24 与膜 23 的第二端相连。在膜 26 的第二端形成通孔导体 27。

如果需要，可重复进行上述陶瓷坯料片 16 和 17 的层叠。

随后，在陶瓷坯料片 18 上，形成钩形导电膜 29 和用于补偿由膜 29 的阶梯状区域造成的空隙的陶瓷坯料层 30。膜 29 的第一端通过插入的通孔导体 27 与膜 26 的第二端相连。形成的膜 29 的第二端伸至陶瓷坯料片 18 的边缘。

钩形导电膜 20、23、26 和 29 干燥后的厚度各约为 30 微米。

在叠合物坯料 13 中(它是将多个包括陶瓷坯料片 14-19 的复合结构层叠而成的)，钩形导电膜 20、23、26 和 29 通过插入通孔的导体 21、24 和 27 彼此依次连接在一起，形成具有多圈的线圈形导体。

图 5 所示构成单块电感器 11 的叠合晶片 12 可通过叠合物坯料 13 烧制而成。图 4 所示的叠合物坯料 13 仅用于制造一片叠合晶片 12。然而，可形成用于制造多片叠合晶片的叠合物坯料。这种情况下，形成叠合物坯料后，将叠合物切割成

片，从而制得许多叠合晶片。

随后，如图 5 所示，在叠合晶片 12 的相反的两端形成外电极 30 和 31，使外电极 30 和 31 分别连接到膜 20 的第一端和膜 29 的第二端，制得单块电感器。

如上面参照图 1-3 所述，陶瓷粉末包含在构成单块陶瓷电容器的陶瓷坯料片 2 和陶瓷坯料层 5 中；并且如上面参照图 4 和 5 所述，陶瓷粉末还包含在构成单块电感器 11 的陶瓷坯料片 14－19 以及陶瓷坯料层 22、25、28 和 30 中。陶瓷粉末的例子包括氧化物陶瓷粉末如氧化铝、氧化锆、氧化镁、氧化钛、钛酸钡、钛酸锆酸铅(lead titanate zirconate)或铁氧体一锰；以及非氧化物陶瓷粉末如碳化硅、氮化硅或硅铝氧氮聚合材料(sialon)。使用的陶瓷粉末较好经粉碎并为球形。粉末的平均粒度较好的为 5 微米或更小，1 微米更好。

当使用含 0.1％(重量)或更小的碱金属氧化物杂质的钛酸钡作为陶瓷粉末时，可以在该陶瓷粉末中加入痕量的下列金属氧化物或玻璃组分。

金属氧化物的例子包括氧化铽、氧化镝、氧化钬、氧化铒、氧化镱、氧化锰、氧化钴、氧化镍、和氧化镁。

玻璃组分的例子包括 $Li_2$-$(SiTi)O_2$-MO(其中 MO 指 $Al_2O_3$ 或 $ZrO_2$)、$SiO_2$-$TiO_2$-MO(其中，MO 指 BaO、CaO、SrO、MgO、ZnO 或 MnO)、$Li_2O$-$B_2O_3$-$(SiTi)O_2$+MO(其中，MO 指 $Al_2O_3$ 或 $ZrO_2$)、$B_2O_3$-$Al_2O_3$-MO(其中，MO 指 BaO、CaO、SrO 或 MgO)、以及 $SiO_2$。

如上面参照图 1-3 所述，使用导电胶形成构成单块陶瓷电容器的内电极 1；如上面参照图 4 和 5 所述，导电胶还用于形成构成单块电感器的钩形导电膜 20、23、26 和 29 以及通孔导体 21、24 和 27。下面描述所用的导电胶。

用于单块陶瓷电容器的导电胶包括铜粉、镍粉、或含 Ag/Pd 合金(比例为 60％(重量)/40％(重量)至 10％(重量)/90％(重量))的导电粉末。这类粉末的平均粒度为 0.02-3 微米，较好为 0.05-0.5 微米。使用三辊磨机捏合该粉末(100 重量份)、有机粘合剂(2－20 重量份，较好的为 5－10 重量份)、作为烧结抑制剂的金属(如 Ag、Au、Pt、Ti、Si、Ni 或 Cu)的树脂酸盐 (约 0.1-3 重量份，较好的为 0.5-1 重量份，折算成金属计)、有机溶剂(约 35 重量份)，随后向形成的混合物中再加入同样或不同的有机溶剂以控制其粘度，从而制得导电胶。

用于单块电感器 11 的导电胶包括含 Ag 或含 Ag/Pd 合金(比例为 80％(重量)/20％(重量)至 100％(重量)/0％(重量))的导电粉末。使用三辊磨机用与上面相同的比例捏合该粉末(100 重量份)和与上面相同的有机粘合剂、烧结抑制剂和有机溶剂，在形成的混合物中再加入同样或不同的有机溶剂以控制其粘度，从而制得

导电胶。

实施例

下面，用试验例更详细地描述本发明。

试验例 1

试验例 1 涉及单块陶瓷电容器。试验例 1 用于确认在制造用于补偿阶梯状区域造成的空隙的陶瓷坯料层的陶瓷糊浆时，第一分散步骤和第二分散步骤的作用。

制造陶瓷粉末

首先，称出碳酸钡($BaCO_3$)和氧化钛($TiO_2$)使之摩尔比为 1:1，并使用球磨机湿混之，形成的混合物脱水并干燥。接着在 1000℃将干的混合物煅烧 2 小时，随后粉碎，制得介电陶瓷粉末。

制备陶瓷淤浆并形成陶瓷坯料片

将 100 重量份如此制得的陶瓷粉末、7 重量份聚乙烯醇缩丁醛(中度聚合产物)、3 重量份作为增塑剂的邻苯二甲酸辛二醇酯(DOP)、30 重量份甲乙酮、20 重量份乙醇、20 重量份甲苯和 600 重量份直径 1mm 的氧化锆磨球放入球磨机中湿磨 20 小时，制得陶瓷淤浆。

用刮刀法将制得的陶瓷淤浆成形成厚度为 3 微米(烧制后为 2 微米)的陶瓷坯料片。在 80℃将该片材干燥 5 分钟。

制造导电胶

使用三辊研磨机捏合 100 重量份金属粉末(Ag/Pd=70/30)、4 重量份乙基纤维素、2 重量份醇酸树脂、3 重量份银金属树脂酸盐(折算成银为 17.5 重量份)和 35 重量份乙酸丁基卡必醇，随后向形成的混合物中加入 35 重量份萜品醇以控制混合物的粘度。

制备用于制造补偿阶梯状区域形成的空隙的陶瓷坯料层的陶瓷糊浆

试样 1

将 100 重量份上面制得的介电陶瓷粉末、70 重量份相对蒸发速率为 465 的

甲乙酮、600 重量份直径为 1mm 的氧化锆磨球放入球磨机湿混 16 小时。接着向该球磨机中加入 40 重量份沸点为 220℃、相对蒸发速率为 10 或更小的萜品醇和 5 重量份乙基纤维素树脂，形成的混合物再混合 16 小时，得到陶瓷淤浆混合物。

随后，使用蒸发器在 60℃的热浴中将上述陶瓷淤浆混合物减压蒸馏 2 小时。通过蒸馏从淤浆中完全除去甲乙酮，得到陶瓷糊浆。随后向陶瓷糊浆中加入 10-20 重量份萜品醇，在自动研钵中分散形成的混合物，从而调节混合物的粘度。

试样 2

将 100 重量份上面制得的介电陶瓷粉末、70 重量份甲乙酮、30 重量份萜品醇、600 重量份直径为 1mm 的氧化锆磨球放入球磨机湿混 16 小时。接着向该球磨机中加入 10 重量份沸点为 220℃的萜品醇和 5 重量份乙基纤维素树脂，形成的混合物再混合 16 小时，得到陶瓷淤浆混合物。

随后，使用蒸发器在 60℃的热浴中将上述陶瓷淤浆混合物减压蒸馏 2 小时。通过蒸馏从淤浆中完全除去甲乙酮，得到陶瓷糊浆。随后向陶瓷糊浆中加入 10-20 重量份萜品醇，在自动研钵中分散形成的混合物，从而控制混合物的粘度。

试样 3

将 100 重量份上面制得的介电陶瓷粉末、70 重量份甲乙酮、0.5 重量份重均分子量为 1000 的聚丙烯酸季铵盐分散剂、600 重量份直径为 1mm 的氧化锆磨球放入球磨机湿混 16 小时。接着向该球磨机中加入 10 重量份沸点为 220℃的萜品醇和 5 重量份乙基纤维素树脂，形成的混合物再混合 16 小时，得到陶瓷淤浆混合物。

随后，使用蒸发器在 60℃的热浴中将上述陶瓷淤浆混合物减压蒸馏 2 小时。通过蒸馏从淤浆中完全除去甲乙酮，得到陶瓷糊浆。随后向陶瓷糊浆中加入 10-20 重量份萜品醇，在自动研钵中分散形成的混合物，从而控制混合物的粘度。

试样 4

将 100 重量份上面制得的介电陶瓷粉末、40 重量份沸点为 220℃的萜品醇和 5 重量份乙基纤维素树脂在自动研钵中进行混合，随后使用三辊研磨机捏合，得到陶瓷糊浆。

制造单块陶瓷电容器

将导电胶网印在上述陶瓷坯料片的一个主表面上，随后在 80℃干燥 10 分钟，形成内电极。确定内电极的大小、形状和位置使之适合下述步骤制得的叠合晶片。接着，将试样 1-4 的各种陶瓷糊浆网印在陶瓷坯料片的该主表面上，接着在 80℃干燥 10 分钟，形成用于补偿阶梯状区域造成的空隙的陶瓷坯料层。干燥后内电极和陶瓷坯料层的厚度为 1 微米，烧制后其厚度为 0.5 微米。

随后将 200 片带有内电极和陶瓷坯料层的陶瓷坯料片叠合在一起，将叠合产物夹在数十片不含内电极的陶瓷坯料片之间，形成叠合物坯料。在 $1000kg/cm^2$ 的压力下在 80℃热压该叠合物坯料。

随后使用割刀将形成的叠合物切成多片叠合晶片。确定各晶片的大小使得烧制后其尺寸为 3.2mm 长×1.6mm 宽×1.6mm 厚。

接着，将上述叠合晶片排列在分布有少量氧化锆粉末的定位器上进行烧制，在 24 小时使晶片的温度由室温升至 250℃，以除去有机粘合剂。随后将形成的晶片放入烧制炉中，在温度最高为 1300℃的温度分布下将该晶片烧制约 20 小时。

接着将形成的烧制晶片放入一圆筒(barrel)，对晶片的侧面进行抛光。然后在烧结晶片的相反表面上形成外电极，制得单块陶瓷电容器作为试样。

评价特性

评价试样 1—4 的各个陶瓷糊浆和单块陶瓷电容器的各种性能。结果列于表 1。

表 1

| 试样 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| 固体含量(重量%) | 65 | 64 | 66 | 67 |
| 粘度(Pa s) | 9 | 8 | 10 | 12 |
| 分散度 | 0 | 0 | -0.2 | 0.3 |
| 网印膜厚度(微米) | 4 | 4 | 3 | 5 |
| Ra(微米) | 0.5 | 0.5 | 0.3 | 1.5 |
| 结构缺陷比例(%) | 2 | 3 | 0 | 80 |

表 1 的特征是如下评价的：

固体含量：精确地称出约 1g 陶瓷糊浆，在将其在 150℃的热对流型烘箱中放置 3 小时。在加热后的糊浆重量的基础上计算糊浆的固体含量。

粘度：陶瓷糊浆的粘度是在 20℃使用转速为 2.5rpm 的 E 型粘度计(Tokyo Keiki 制)测定的。

分散度：使用光折射粒径分布测量装置测定陶瓷粉末的粒径分布，在测定数据的基础上计算粉末的分散度。简单地说，使用超声波匀化器将上面制得的陶瓷粉末分散在水中，对该颗粒施加超声波直至其尺寸降至最小。当颗粒达到其最小尺寸时，记录 D90 粒径分布的粒径作为“极限粒径”。另外，用乙醇稀释陶瓷糊浆，将其 D90 粒径分布的粒径记录为“糊浆粒径”。用下列公式计算陶瓷粉末的分散度：

分散度=(糊浆粒径/极限粒径)－1

在分散度呈正值的情况下，该值越接近 0，则粉末的分散性越高。相反，在分散度呈负值的情况下，其绝对值越大，则粉末的分散性越高。

网印膜的厚度：使用厚度为 50 微米的 400 目不锈钢丝网将陶瓷糊浆涂覆在 96％氧化铝基片上，形成的基片在 80℃干燥 10 分钟，形成网印膜用于评价。使用非接触式激光表面粗糙度测量仪测定该膜的厚度。

表面粗糙度(Ra)：用与上面相同的方法形成网印膜用于评价。使用非接触式激光表面粗糙度测量仪测得的数据得到膜的表面粗糙度(Ra)，即波动平均中心线和粗糙度曲线偏差的绝对值的平均值。

结构缺陷比例：用超声波显微镜和肉眼观察用于制造单块陶瓷电容器的烧制晶片。当晶片抛光后观察到异常部分时，则确认晶片具有内部结构缺陷。用下列公式算得结构缺陷的比例：具有结构缺陷的烧结晶片数/烧结晶片总数。

由表 1 可见，试样 1-3 的陶瓷糊浆和电容器(实施第一和第二分散步骤，并且在第二分散步骤过程中加入有机粘合剂)与试样 4 的陶瓷糊浆和电容器(不实施所述步骤)相比具有优良的分散性、网印膜厚度、表面粗糙度和结构缺陷比例这些特性。

试验例 2

试验例 2 也涉及单块陶瓷电容器。试验例 2 确认在制造用于补偿阶梯状区域造成的空隙的陶瓷坯料层的陶瓷糊浆过程中增加过滤步骤的影响。

重复试验例 1 的步骤，但是如下面所述实施“制造用于补偿阶梯状区域造成的空隙的陶瓷坯料层的陶瓷糊浆”的步骤，从而制得单块陶瓷电容器。

制造用于补偿阶梯状区域造成的空隙的陶瓷坯料层的陶瓷糊浆

试样 5

使用绝对过滤精度为 20 微米的过滤器(即用该过滤器除去大小为 10 微米或更大的物质的几率为 99.7%)加压过滤用与试验例 1 的试样 1 相同的方法制得的陶瓷糊浆混合物。

接着，用与试验例 1 的试样 1 相同的方法处理形成的陶瓷糊浆混合物，得到陶瓷糊浆。

试样 6

重复试样 5 的制造步骤，但是在完成用绝对过滤精度为 20 微米的过滤器进行过滤后，再用绝对过滤精度为 1 微米的过滤器加压过滤之，得到陶瓷糊浆。

试样 7

用行星式搅拌器混合 40 重量份沸点为 220℃的萜品醇、10 重量份甲乙酮和 5 重量份乙基纤维素树脂，制得有机载体。随后用绝对过滤精度为 20 微米的过滤器加压过滤该有机载体。

另外，将 100 重量份上面制得的介电陶瓷粉末、60 重量份甲乙酮、600 重量份直径为 1mm 的氧化锆磨球放入球磨机中湿磨 16 小时。

接着，将上述经过滤的有机载体加至该球磨机中，将形成的混合物再混合 16 小时，制得陶瓷淤浆混合物。

用与试验例 1 的试样 1 相同的方法对该陶瓷淤浆混合物进行加工，得到陶瓷糊浆。

试样 8

重复试样 7 的制造步骤，但是在完成用绝对过滤精度为 20 微米的过滤器进行过滤后，再用绝对过滤精度为 1 微米的过滤器加压过滤之，得到陶瓷糊浆。

试样 9

重复试样 7 的制造步骤，并用与试样 5 相同的方法进一步过滤该陶瓷淤浆混合物，得到陶瓷糊浆。

评价试样 5-9 的各种陶瓷糊浆和单块陶瓷电容器的各种特性。结果列于表 2。

表 2

| 试样 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|
| 固体含量(重量%) | 66 | 67 | 66 | 67 | 68 |
| 粘度(Pa s) | 10 | 12 | 15 | 14 | 16 |
| 分散度 | -0.1 | -0.2 | 0 | 0 | -0.3 |
| 网印膜厚度(微米) | 3 | 2 | 3 | 2 | 2 |
| Ra(微米) | 0.4 | 0.3 | 0.5 | 0.5 | 0.2 |
| 结构缺陷比例(%) | 1.5 | 1 | 1.5 | 1 | 0 |

表 2 所示特性的评价方法与表 1 所示特性的评价方法相同。

表 2 的试样 5 与表 1 的试样 1 的不同之处在于试样 5 的陶瓷淤浆混合物经过过滤。因此，比较试样 5 和试样 1 就可得知过滤的效果。也就是说，与试样 1 的陶瓷糊浆和电容器的比较表明，试样 5 的陶瓷糊浆和电容器表现出优良的分散性、网印膜厚度、表面粗糙度和结构缺陷比例的特性。

由表 2 所示，通过比较试样 5 和试样 6、试样 7 和试样 8、试样 5 和试样 9 以及试样 7 和试样 9 可见，当重复进行过滤或者组合进行不同类型的过滤时，可进一步增强效果。

试验例 3

试验例 3 也涉及单块陶瓷电容器。进行试验例 3 以确认在制造用于补偿阶梯状区域造成的空隙的陶瓷坯料层的陶瓷糊浆时，第一和第二有机溶剂的较好相对蒸发速率范围。

重复试验例 1 的步骤，但是如下所述进行“制造用于补偿阶梯状区域造成的空隙的陶瓷坯料层的陶瓷糊浆”的步骤，制得单块陶瓷电容器。

制造用于补偿阶梯状区域造成的空隙的陶瓷坯料层的陶瓷糊浆

试样 10

重复试验例 1 的试样 1 的制造步骤，但是使用相对蒸发速率为 100 的乙酸正丁酯作为第一有机溶剂，制得陶瓷糊浆。

试样 11

重复试验例 1 的试样 1 的制造步骤，但是使用相对蒸发速率为 720 的丙酮作为第一有机溶剂，制得陶瓷糊浆。

试样 12

重复试验例 1 的试样 1 的制造步骤，但是使用相对蒸发速率为 83 的异丁醇作为第一有机溶剂，制得陶瓷糊浆。

试样 13

重复试验例 1 的试样 1 的制造步骤，但是使用相对蒸发速率为 370 的甲醇作为第一有机溶剂，将相对蒸发速率为 55 的甲基溶纤剂作为第二有机溶剂，制得陶瓷糊浆。

评价各个试样 10-13 的陶瓷糊浆和单块陶瓷电容器的各种特性。结果列于表 3。表 3 还列出了试样 10-13 使用的第一和第二有机溶剂。

表 3

| 试样 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|
| 第一有机溶剂(相对蒸发速率) | 乙酸正丁酯(100) | 丙酮(720) | 异丁醇(83) | 甲醇(370) |
| 第二有机溶剂(相对蒸发速率) | 萜品醇(10 或更小) | 萜品醇(10 或更小) | 萜品醇(10 或更小) | 甲基溶纤剂(55) |
| 蒸发时间(小时) | 2 | 1 | 4 | 蒸发持续长时间 |
| 固体含量(重量%) | 70 | 67 | 66 | — |
| 粘度(Pa s) | 15 | 9 | 10 | — |
| 分散度 | 0.2 | 0 | 0.4 | - |
| Ra(微米) | 0.7 | 0.5 | 1.0 | - |
| 结构缺陷比例(%) | 3 | 2 | 10 | - |

在表 3 中，“蒸发时间”栏是指在减压下开始蒸发至有机溶剂(通常第一有机溶剂)蒸发结束之间的时间。除“蒸发时间”以外表 3 所示特性的评价方法与表 1 所用的方法相同。

由表 3 可见，在试样 10 和 11 中，在短时间内第一有机溶剂蒸发完全，因为第一有机溶剂的相对蒸发速率为 100 或更高，而第二有机溶剂的相对蒸发速率为 50 或更低。另外，试样 10 和 11 的陶瓷糊浆和电容器表现出优良的分散性、表面粗糙度和结构缺陷比例的特性。

相反，在试样 12 中，第一有机溶剂的蒸发不能在短时间内完成，因为第一有机溶剂的相对蒸发速率小于 100，尽管第二有机溶剂的相对蒸发速率为 50 或更

低。与试样 10 和 11 相比，试样 12 的陶瓷糊浆和电容器表现出差的分散性、表面粗糙度和结构缺陷比例的特性。

试样 13 的第二有机溶剂的蒸发持续较长的时间，因为第二有机溶剂的相对蒸发速率超过 50，尽管第一有机溶剂的相对蒸发速率为 100 或更高。在这种情况下，在网印过程中陶瓷糊浆快速干燥，因此印网不合需求地带有糊浆，导致网印性差。

试验例 4

试验例 4 涉及单块电感器。实施试验例 4 确认第一和第二分散步骤在制造用于补偿阶梯状区域导致的空隙的陶瓷坯料层的陶瓷糊浆中的影响。

制造陶瓷粉末

称重氧化铁粉末、氧化锌粉末、氧化镍粉末、和氧化铜粉末使之比例分别为 49.0 重量%、29.0 重量%、14.0 重量%、和 8.0 重量%。使用球磨机湿混这些粉末并脱水干燥形成的混合物。将干燥的混合物在 750℃烧结 1 小时后，粉碎之，得到磁性陶瓷粉末。

制备陶瓷淤浆并形成陶瓷坯料片

将 100 重量份如此制得的磁性陶瓷粉末、7 重量份聚乙烯醇缩丁醛(中度聚合产物)、3 重量份作为增塑剂的邻苯二甲酸二辛酯(DOP)、30 重量份甲乙酮、20 重量份乙醇、20 重量份甲苯和 600 重量份直径 1mm 的氧化锆磨球放入球磨机中湿磨 20 小时，制得陶瓷淤浆。

用刮刀法将制得的陶瓷淤浆成形成厚度为 20 微米(烧制后为 15 微米)的陶瓷坯料片。在 80℃将该片材干燥 5 分钟。

制造导电胶

使用三辊研磨机捏合 100 重量份金属粉末(Ag/Pd=70/30)、4 重量份乙基纤维素、2 重量份醇酸树脂、3 重量份银金属树脂酸盐(折算成银为 17.5 重量份)和 35 重量份乙酸丁基卡必醇酯，随后向形成的混合物中加入 35 重量份萜品醇以控制混合物的粘度。

制备用于制造补偿阶梯状区域形成的空隙的陶瓷坯料层的陶瓷糊浆

试样 14

将 100 重量份上述磁性陶瓷粉末、70 重量份相对蒸发速率为 465 的甲乙酮、600 重量份直径为 1mm 的氧化锆磨球放入球磨机湿混 16 小时。接着向该球磨机中加入 40 重量份沸点为 220℃、相对蒸发速率为 10 或更小的萜品醇和 5 重量份乙基纤维素树脂，形成的混合物再混合 16 小时，得到陶瓷淤浆混合物。

随后，使用蒸发器在 60℃的热浴中将上述陶瓷淤浆混合物减压蒸馏 2 小时。通过蒸馏从淤浆中完全除去甲乙酮，得到陶瓷糊浆。随后向陶瓷糊浆中加入 10-20 重量份萜品醇，在自动研钵中分散形成的混合物，从而调节混合物的粘度。

试样 15

将 100 重量份上述磁性陶瓷粉末、70 重量份甲乙酮、30 重量份萜品醇、600 重量份直径为 1mm 的氧化锆磨球放入球磨机湿混 16 小时。接着向该球磨机中加入 10 重量份沸点为 220℃的萜品醇和 5 重量份乙基纤维素树脂，形成的混合物再混合 16 小时，得到陶瓷淤浆混合物。

随后，使用蒸发器在 60℃的热浴中将上述陶瓷淤浆混合物减压蒸馏 2 小时。通过蒸馏从淤浆中完全除去甲乙酮，得到陶瓷糊浆。随后向陶瓷糊浆中加入 10-20 重量份萜品醇，在自动研钵中分散形成的混合物，从而控制混合物的粘度。

试样 16

将 100 重量份上面制得的磁性陶瓷粉末、70 重量份甲乙酮、0.5 重量份重均分子量为 1000 的聚丙烯酸季铵盐分散剂、600 重量份直径为 1mm 的氧化锆磨球放入球磨机湿混 16 小时。接着向该球磨机中加入 10 重量份沸点为 220℃的萜品醇和 5 重量份乙基纤维素树脂，形成的混合物再混合 16 小时，得到陶瓷淤浆混合物。

随后，使用蒸发器在 60℃的热浴中将上述陶瓷淤浆混合物减压蒸馏 2 小时。通过蒸馏从淤浆中完全除去甲乙酮，得到陶瓷糊浆。随后向陶瓷糊浆中加入 10-20 重量份萜品醇，在自动研钵中分散形成的混合物，从而控制混合物的粘度。

试样 17

将 100 重量份上面制得的磁性陶瓷粉末、40 重量份沸点为 220℃的萜品醇和 5 重量份乙基纤维素树脂在自动研钵中进行混合，随后使用三辊研磨机捏合，得

到陶瓷糊浆。

制造单块电感器

在上面制得的磁性陶瓷坯料片的预定位置形成用于填充通路孔导体的孔，以便在多层片材叠合后能形成线圈状导体。将导电胶涂覆在所述磁性陶瓷坯料片上，随后在80℃干燥10分钟，在坯料片的主表面上形成钩状导电膜并在所述孔中形成通孔导体。接着，将试样14-17的各种磁性陶瓷糊浆施涂在磁性陶瓷坯料片上，在80℃干燥10分钟，形成用于补偿阶梯状区域造成的空隙的磁性陶瓷坯料层。干燥后钩状导电膜和陶瓷坯料层的厚度为30微米，烧制后其厚度为20微米。

随后将11片带有钩状导电膜、通孔导体和陶瓷坯料层的磁性陶瓷坯料片叠合在一起，在得到的叠合产物内形成线圈状导体。随后将叠合产物夹在不含钩状导电膜的磁性陶瓷坯料片之间，形成叠合物坯料。在1000kg/cm$^2$的压力下在80℃热压该叠合物坯料。

随后使用割刀将形成的叠合物切成多片叠合晶片。确定各晶片的大小使得烧制后其尺寸为3.2mm长×1.6mm宽×1.6mm厚。

接着，将上述叠合晶片在400℃加热2小时，以除去有机粘合剂，随后将得到的晶片在900℃烧制90分钟。

将形成的烧制晶片放入一圆筒(barrel)，对晶片的侧面进行抛光。在烧结晶片的相反表面上形成主要由银制成的外电极，制得晶片型单块电感器作为试样。

评价特性

评价试样14—17的各个陶瓷糊浆和单块电感器的各种性能。结果列于表4。

表 4

| 试样 | 14 | 15 | 16 | 17 |
|---|---|---|---|---|
| 固体含量(重量%) | 72 | 73 | 72 | 73 |
| 粘度(Pa s) | 15 | 14 | 17 | 18 |
| 分散度 | 0 | 0 | -0.3 | 0.2 |
| 网印膜厚度(微米) | 20 | 21 | 19 | 19 |
| Ra(微米) | 0.5 | 0.5 | 0.2 | 1.6 |
| 结构缺陷比例(%) | 1 | 1 | 0 | 50 |

用于评价表4所示特性的方法与表1所用的方法相同。

由表 4 可见，试样 14-16 的陶瓷糊浆和电感器(实施第一和第二分散步骤，并且在第二分散步骤过程中加入有机粘合剂)与试样 17 的陶瓷糊浆和电感器(不实施所述步骤)相比具有优良的分散性、网印膜厚度、表面粗糙度和结构缺陷比例这些特性。这些结果与表 1 所示的试验例 1 的结果相同。

上面描述了在将介电陶瓷粉末或磁性陶瓷粉末加入本发明陶瓷糊浆的例子。但是，在本发明中，陶瓷糊浆的特性不受这些糊浆所含的陶瓷粉末的电气特性的影响。因此，含有绝缘陶瓷粉末或压电陶瓷粉末的陶瓷糊浆具有与含介电陶瓷粉末或磁性陶瓷粉末的陶瓷糊浆相同的特性。

如上所述，本发明陶瓷糊浆是由下列步骤制得的：第一分散步骤，该步骤对含有陶瓷粉末和第一有机溶剂的第一混合物进行初次分散；第二分散步骤，该步骤对含有有机粘合剂和经第一分散步骤处理的第一混合物进行二次分散；将相对蒸发速率低于第一有机溶剂的相对蒸发速率的第二有机溶剂加至第一混合物和/或第二混合物的步骤；以及通过加热第二混合物从其中选择性地除去第一有机溶剂的步骤。结果，可进一步增强陶瓷糊浆所含陶瓷粉末的分散性。因此，该陶瓷糊浆可有利地用于形成具有高图案精度的很薄的陶瓷坯料层。

根据本发明，由于使用陶瓷糊浆在陶瓷坯料片主表面上未形成内线路元件薄膜的区域形成陶瓷坯料层，从而基本补偿所述薄膜形成的阶梯状区域导致的空隙，因此形成的单块陶瓷电子元件无结构缺陷，如开裂和脱层，并显示出高的可靠性。

根据本发明，可令人满意地减小单块陶瓷电子元件的尺寸和重量。因此，当将本发明用于单块陶瓷电容器时，可有利地降低该电容器的尺寸并可有利地增加该电容器的电容。另外，当将本发明用于单块电感器时，可有利地降低该电感器的尺寸并可有利地提高其电感。

当在上述第一分散步骤过程中将有机分散剂加入第一混合物中时，可进一步提高陶瓷粉末的分散性。

当第一有机溶剂在 20℃的相对蒸发速率为 100 或更高，并且第二有机溶剂在 20℃的相对蒸发速率为 50 或更低时，在除去步骤中可容易地除去第一有机溶剂，另外可使网印容易进行。

在第二分散步骤后但在除去步骤前对第二混合物进行过滤，或者将有机粘合剂溶解在第一有机溶剂和/或第二有机溶剂以形成有机载体，并对有机载体进行过滤再加至第二混合物中，可除去陶瓷糊浆中存在的杂质、陶瓷粉末絮凝物和不溶解的有机粘合剂，从而可可靠地增强陶瓷糊浆的分散性。另外，可减少形成的

陶瓷层中的针孔数。

可选择第一和第二有机溶剂使得第一有机溶剂的相对蒸发速率高于第二有机溶剂的相对蒸发速率。因此，当选择第一和第二有机溶剂使得第一有机溶剂的沸点低于第二有机溶剂的沸点时，就可容易地选择这些溶剂。

在根据沸点差异选择第一和第二有机溶剂时，当第一有机溶剂的沸点与第二有机溶剂的沸点相差 50° 或更大时，在完成第二分散步骤后可通过加热容易地选择性除去第一有机溶剂。

在本发明单块陶瓷电子元件的制造方法中，当用于形成陶瓷坯料片的陶瓷淤浆所含的陶瓷粉末的组成与用于形成陶瓷坯料层的陶瓷糊浆所含的陶瓷粉末的组成基本相同时，可均匀地烧结陶瓷坯料片和用于补偿阶梯状区域造成的空隙的陶瓷坯料层。当均匀烧结陶瓷坯料片和陶瓷坯料层时，可防止开裂和脱层。

# 说 明 书 附 图

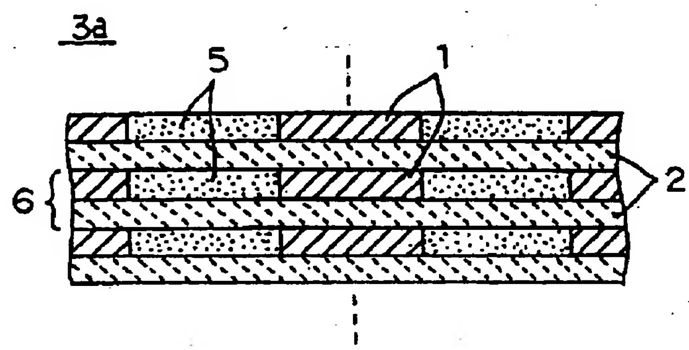


图 1

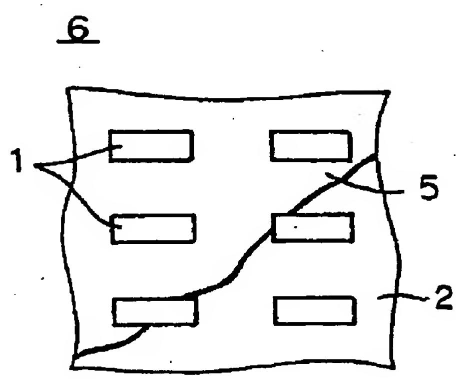


图 2

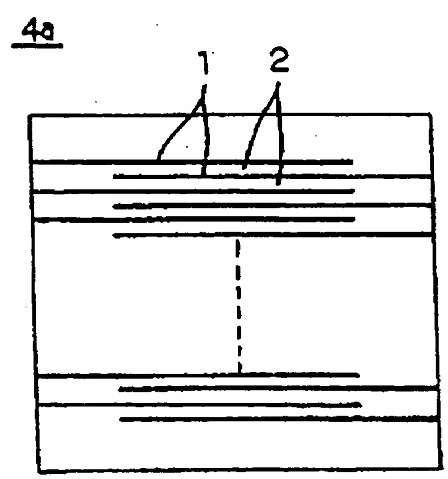


图 3

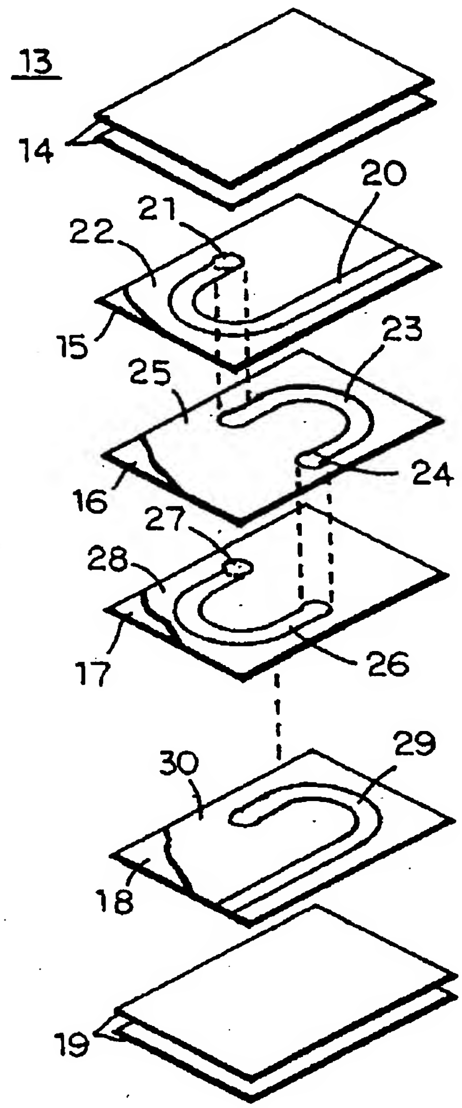


图 4

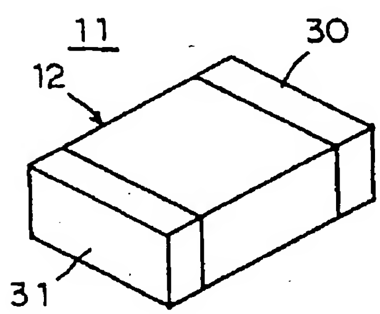


图 5

3

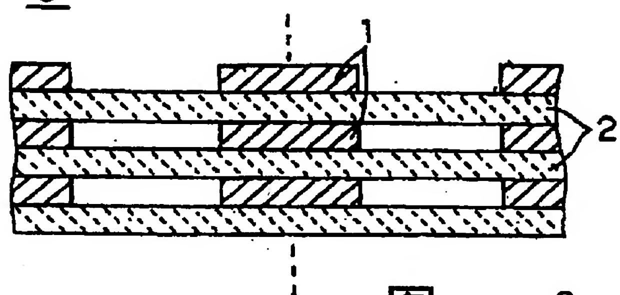


图 6

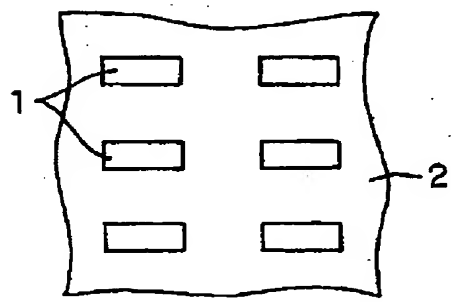


图 7

4

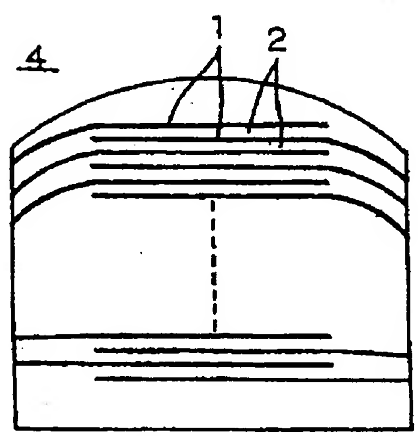


图 8